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**D'Orbigny: A non-igneous angritic achondrite?**G. KURAT,<sup>1,\*</sup> M. E. VARELA,<sup>2</sup> F. BRANDSTÄTTER,<sup>1</sup> G. WECKWERTH,<sup>3</sup> R. N. CLAYTON,<sup>4</sup> H. W. WEBER,<sup>5</sup>  
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**Abstract**—D'Orbigny is the sixth and by far the largest angrite known. Its bulk chemical and mineral chemical compositions, rare gas abundances and oxygen and rare gas isotope compositions fit the compositional ranges known from other angrites. It is, however, peculiar with respect to three features: the abundance of hollow shells, the presence of abundant open druses and the abundant presence of glasses.

The shape, structure and texture of D'Orbigny and its mineral and bulk chemical compositions indicate an unusual genesis under changing redox conditions. In our view, data and observations are incompatible with an igneous origin of this rock but are suggestive of a complex growth and metasomatism scenario. The sequence of events apparently began with the formation of spheres of a phase which later vanished and therefore is unknown but could have been CaS. On top of these spheres (sizes from < 1–30 mm) olivine-anorthite intergrowths precipitated forming compact shells and fluffy protrusions. Aggregation of these objects plus occasional large plates made of the same intergrowths led to formation of a highly porous object with abundant large open space between the olivine-anorthite intergrowths. The aggregate also included previously formed olivines, olivinite rocks and Al-spinels. The latter carry highly porous decomposition rims of Cr-enriched Al-spinel and record mildly oxidizing conditions prevailing very early in D'Orbigny's history. Conditions changed (with falling T?) and became oxidizing causing the phase(s) that constituted the spheres to become unstable. Their breakdown liberated large amounts of Ca and trace elements which at least in part re-precipitated by reacting with Si and Mg from the vapor to form augites that grew into the open space thus forming augite druses. Also, some of the preexisting olivine was converted into augite, which is very rich in refractory lithophile trace elements (abundances ~ 10 × CI). Augites grew mainly under oxidizing conditions leading to atomic Fe/(Fe+Mg) ratios of about 0.44. Finally, conditions became highly oxidizing and strongly mobilized Ca from a source that apparently became unstable. The high partial pressures of Ca and Fe (and also Ti) led to precipitation of Ca-olivine and kirschsteinite (~Fo1La20 and ~Fo1La33, respectively) and of titaniferous aluminous hedenbergite—atomic Fe/(Fe+Mg) ~ 0.97. Ulvöspinel and sulfides were also precipitated. Because the original phase(s) forming the early spheres vanished during these oxidizing events, the shells remained empty.

In this scenario, D'Orbigny provides us with a record of changing conditions ranging from extremely reducing to highly oxidizing and with a record of the formation of an achondritic rock from a chondritic source. Angrites bear many similarities with CAIs, texturally, mineralogically and chemically. Possibly, they can be seen as CAIs, which grew larger than the ones we know from carbonaceous chondrites. Thus, angrites may bear a record of rare and special conditions in some part of the early solar nebula. They reproduce most of the textures and structures of CAIs: crystallized liquids (Asuka 881371, LEW 87051), metasomatic granoblastic rocks (LEW 86010, Angra dos Reis?) and aggregates (D'Orbigny). In addition, all angrites record metasomatic alterations, subsolidus processing after formation, also similar to what is recorded by most CAIs. Obviously, they missed the alkali metasomatic event recorded by many CAIs but they record a siderophile—lithophile element separation event that is not recorded by CAIs. Copyright © 2004 Elsevier Ltd

**1. INTRODUCTION**

Angrites are very rare meteorites forming a group of only five members (Koblitz, 2003). D'Orbigny, found in the Buenos Aires province of Argentina, is the sixth angrite known up to now (Table 1), and the largest and gives us a wonderful opportunity to study in detail the origin of these enigmatic

rocks. Although widely believed to be igneous rocks, angrites have many primitive features and chemical and mineralogical properties which are highly unusual for igneous rocks. They are very old, similar to chondrites. U-Pb, Th-Pb and Pb-Pb ages for Angra dos Reis and LEW 86010 are between 4.54 and 4.5578 Ga (Wasserburg et al., 1977; Lugmair and Galer, 1992). Sm-Nd ages are 4.55 Ga (Lugmair and Marti, 1977 —Angra dos Reis), 4.56 Ga (Jacobsen and Wasserburg, 1984 —Angra dos Reis) and 4.55 and 4.53 Ga for LEW 86010 as determined by Lugmair and Galer (1992) and Nyquist et al. (1994), respec-

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Table 1. The angrites: an overview (CREA = cosmic ray exposure age; ol. = olivine; M-crysts = megacrysts).

Meteorite	Mass kg	Date fall/find;	Country	Subtype	Comments (references);
Angra dos Reis	1.5	1869	Brazil	Pyroxenitic	CREA 55.5 Ma (3, 4);
Asuka 881371	0.0112	1988	Antarctica	Basaltic	CREA 5.3 Ma, ol. xenocrysts (1, 2, 3);
D'Orbigny	16.55	1979	Argentina	Basaltic	CREA 11 Ma, ol. M-crysts, druses, shells, plates;
LEW 86010	0.0069	1986	Antarctica	Basaltic	CREA 17.6 Ma (3);
LEW 87051	0.0006	1987	Antarctica	Basaltic	CREA >~0.2 Ma, ol. xenocrysts (3);
SAHARA 99555	2.71	1999	N-Africa	Basaltic	CREA 6.1 Ma, shells (5);

- 1: Yanai (1994).
- 2: Prinz and Weisberg (1995).
- 3: Eugster and Weigel (1995).
- 4: Ludwig and Tschermak (1909).
- 5: Bischoff et al. (2000)

tively. Angrites also contain daughter nuclei of short-lived, now extinct isotopes like excesses in  $^{142}\text{Nd}$  (Lugmair and Marti, 1977; Jacobsen and Wasserburg, 1984; Lugmair and Galer, 1992; Nyquist et al., 1994), in  $^{53}\text{Cr}$  (Nyquist et al., 1994, 2003) and fission xenon from short-lived  $^{244}\text{Pu}$  (Hohenberg, 1970; Lugmair and Marti, 1977; Wasserburg et al., 1977; Eugster et al., 1991; Hohenberg et al., 1991).

The mineralogical composition of angrites is unusual. It is highly refractory and yet very rich in FeO. All phases are usually out of equilibrium. Ferroan, aluminous and titaniferous augite coexists with anorthite, Mg-rich olivine, Ca, Fe-rich olivine, kirschsteinite, a variety of oxides, phosphates, sulfides and some Ni, Fe metal (Prinz et al., 1977, 1988, 1990; Goodrich, 1988; McKay et al., 1988, 1990, 1995; Prinz and Weisberg, 1995; Mikouchi et al., 1996; Yanai 1994). Furthermore, Fe-poor and Fe-rich olivines coexist as does aluminous hedenbergite with aluminous, less Fe-rich augite.

The chemical composition of angrites is peculiar as well, with high abundances of refractory lithophile elements (~10–15 × CI carbonaceous chondrite abundances—in the following shortened to “CI”) and low abundances of siderophile and volatile elements (see summary by Mittlefehldt et al., 1998). Elemental abundances of refractory elements are practically unfractionated with respect to solar abundances at the 10× to 15× CI level, very similar to those in eucrites and in Ca, Al-rich inclusions in carbonaceous chondrites (Prinz et al., 1988, 1990; Prinz and Weisberg, 1995). In contrast to all other angrites, Angra dos Reis (ADOR) has trace element abundances that are not only high but also fractionated. This is a clear sign that ADOR cannot be a cumulate rock from a parental liquid of basaltic angrite composition because such a clinopyroxene cumulate should be poorer in trace elements than the parental liquid. The fractionated trace element pattern, however, is no surprise for a mono-mineralic rock, but the deficit in Sc is a surprise as Sc can be expected to be enriched in pyroxenites with respect to other refractory lithophile elements. Thus, elements expected to be enriched in the presumed cumulate rock ADOR are depleted and those expected to be depleted (the incompatible elements) are enriched with respect to their abundances in the possible parent (basaltic angrite). Clearly, the relationship between ADOR and the basaltic angrites must be one that differs fundamentally from that of a simple igneous cumulate-parent.

Another peculiarity is the combination of highly refractory elements with oxidized Fe, MnO and some S, accompanied by

a strong depletion of other cosmochemically moderately volatile elements such as Na and K. Clearly, there is no simple way to create this class of rocks, a fact previously recognized by Prinz et al. (1988, 1990), Prinz and Weisberg (1995) and Longhi (1999). There are two unsolved problems with an igneous origin of angrites: 1) Creating a liquid of such an unusual (basaltic angrite) composition and 2) producing the observed mineralogy and mineral composition from such a liquid. We shall add another one: the unusual structure and texture of D'Orbigny.

Considering all these well-known facts, it is surprising that the belief in an igneous origin of angrites is still widespread. This study aims at providing a new view on angrites. Beside mineralogical, chemical and isotope data we will also describe and discuss the shape of D'Orbigny and its structure, both of which are peculiar. Thanks to the co-operation of the owner of D'Orbigny we had the opportunity to investigate this unusual rock in detail and in an unusual way. We were, for the first time, able to investigate a complete large angrite in three dimensions. The result is astonishing and will hopefully provide some momentum to the study of angrites.

Preliminary reports of our work on D'Orbigny have been presented at conferences (Kurat et al., 2001a, 2001b, 2001c, 2003a; Varela et al., 2001a, 2001b, 2003a; Eugster et al., 2002; Jagoutz et al., 2002a, 2002b, 2003; Jotter et al., 2002, 2003; Kubny et al., 2002, 2003).

## 2. LOCALITY AND CIRCUMSTANCES OF FIND

D'Orbigny, a piece of 16.55 kg, was found in July 1979 during plowing a rock-free field in the south of the Buenos Aires Province, Argentina (37°40'S, 61°39'W). The soil of this area is clayish with calcareous hardpan (calcrete called “tosca”) forming near the surface here and there. The nearest place where some real rocks (granites, gneisses) occur is more than 100 km away. Consequently, whenever stones are found in this region, it is assumed that they are Indian artifacts. As during the XIX<sup>th</sup> century this farm was sort of a frontier between the big farms protected by small forts and Indian territory it is quite common that stony objects manufactured by Indians, such as arrow points, spears, mortars, knives, etc., are found. Because of this and because of its shape D'Orbigny was believed to be an Indian artifact, in particular a mortar, and was kept at the farm. When the owner of the land saw the piece he suspected that it might be a meteorite because of the radial flow lines on

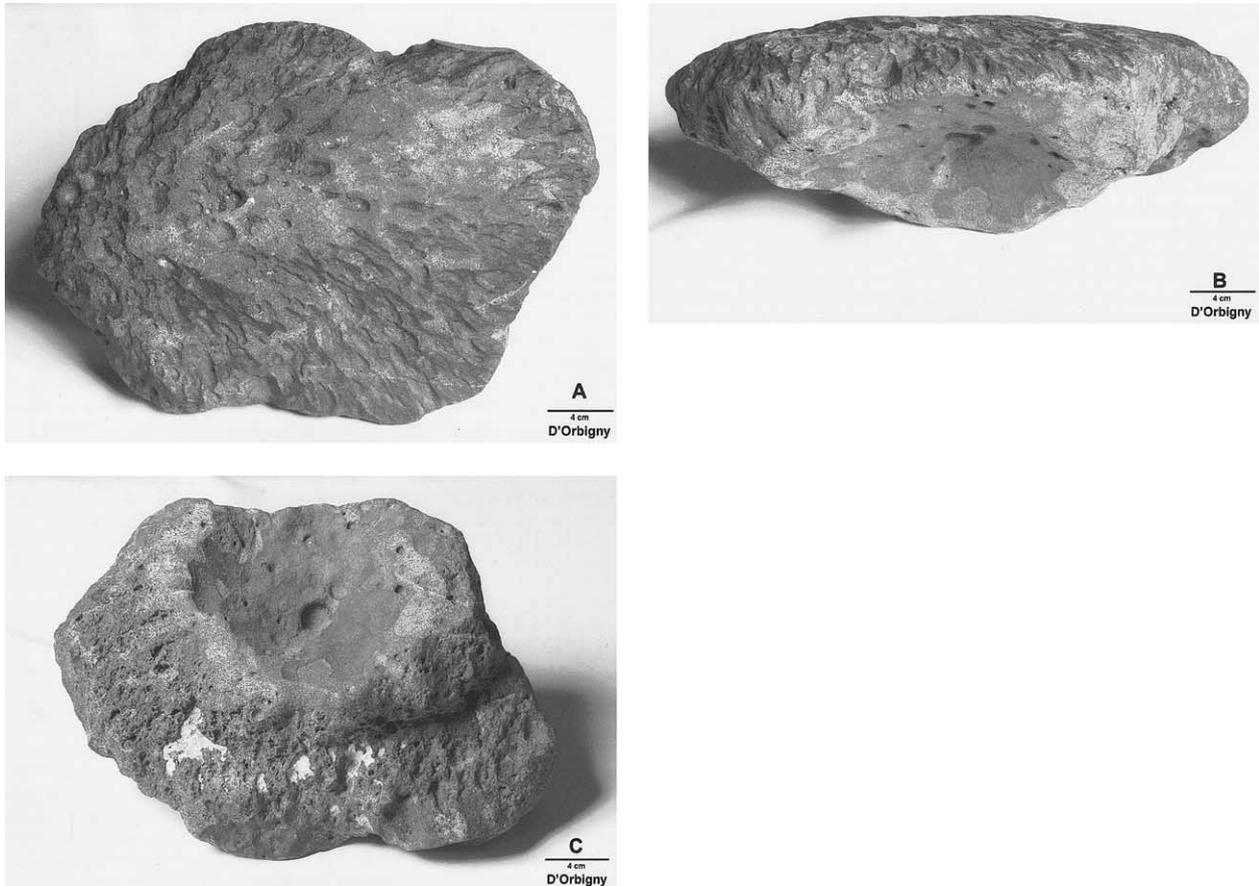


Fig. 1. The D'Orbigny angrite as it was found. (A) Front shield with elongated regmaglypts pointing radially from the stagnation point (center left) and open round vugs of variable sizes. Scars and partly removed fusion crust from plow. Specimens for first identification and bulk analysis were taken from compact lithology of the front shield at upper right (visible cut). (B) Side view at lower part in (A) showing the edge at which the front shield and the back side pan, both consisting of compact rock, are intergrown. Note the open round vugs and the porous lithology to the right and left of the pan (large irregularly shaped open spaces). Pan and shield are covered by fusion crust, edges are worn and without fusion crust. (C) Inclined view at back side pan from upper side in (A), opposite side from (B), depicting the pan and the porous lithology situated between the compact shield and pan lithologies. Note the abundant irregularly shaped open space, some of which is partly filled by caliche (white). Length of the meteorite was 34 cm.

its convex face which is almost totally covered by a fusion crust. However, it was 20 yr later only, when a sample was sent to Vienna and that stone was identified as an angrite.

### 3. ANALYTICAL METHODS

To avoid contamination we broke the meteorite open with a heavy hydraulic press, the smaller pieces with a laboratory hydraulic press. Fragments were studied with a hand lens and samples of the different lithologies were taken. Polished mineral mounts and thin sections were studied by optical microscopy, analytical scanning electron microscopy and phases were analyzed using an ARL-SEMQ microprobe (Naturhistorisches Museum, Wien) operated at 15 kV acceleration potential and 15 nA sample current. A Nonius KappaCCD diffractometer (Institut für Mineralogie und Kristallographie, Universität Wien) was used to verify the amorphous nature of a glass sample and to investigate fine-grained olivinites. Major and trace element abundances were determined by instrumental neutron activation (INAA) at the Institut für Mineralogie, Universität zu Köln. Concentration and isotopic composition of noble gases were determined in a bulk sample at the Max-Planck-Institut für Chemie, Mainz, following procedures described by Schultz and Weber (1996). Oxygen isotope abundances were measured in a bulk sample at

the University of Chicago following the procedures of Clayton and Mayeda (1983).

## 4. RESULTS

### 4.1. Shape and Structure

D'Orbigny, as it was found, had a somewhat unusual shape (Fig. 1). As a typical oriented-flight stone it had a front shield (~ 38 cm long) which gently sloped from the stagnation point which was located off-center. The surface had abundant regmaglypts and was covered by a dark brown fusion crust. The back side had a much smaller diameter (~ 20 cm) and consisted of a concave, round, pan-like indentation with a marked large (~ 2 cm) and several smaller, round open vugs (Fig. 1C). It was also covered by fusion crust and had only weakly developed regmaglypts. The meteorite had a peculiar shape, somewhat like a loaf of bread, with the front and back shields being curved in a semiparallel way and being intergrown on one side with the opposite side opening like a clam (Fig. 1B and

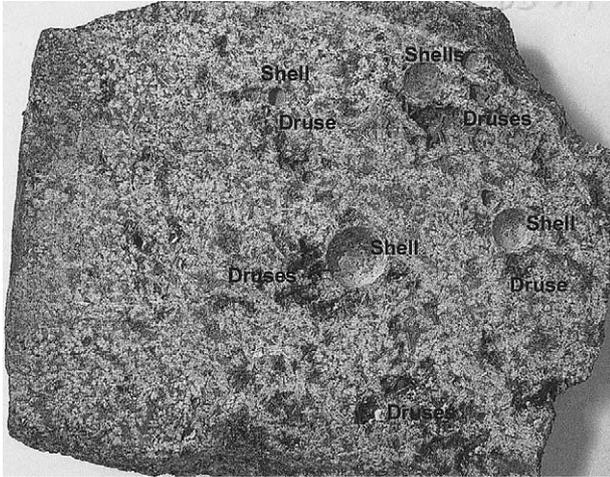


Fig. 2. Slice cut perpendicular to front surface (left) depicts the compact lithology of the shield and the porous lithology of the inside of D'Orbigny. Plagioclase is gray, olivine and augite are dark gray and druse augite is black. Note the difference between these two lithologies in grain-size, texture, abundance of hollow shells and of druses (dark) and the complex transition between shield and interior. Note also the association of shells and druses. Width of picture is ~ 8 cm.

1C, respectively). The space between the plates was filled by a highly porous lithology, very rich in open voids and hollow spheres, partly filled by caliche, well visible in Figure 1C.

The large irregular open voids were highly elongated with the major axis roughly aligned radially from the back side pan-like plate. Openings had dimensions up to about 1 cm width and 7 cm length. Many of the originally exposed large voids had the walls covered by fusion crust and were partly filled by caliche. Most of the small irregular voids had the walls covered by shiny black augite crystals. All freshly broken open voids (Fig. 2) had the walls covered by black shiny pyroxene crystals (from now on we shall call these voids druses), occasionally covered by some caliche or by a rusty red film, presumably humic acids, and some iron oxide/hydroxide from the local soil.

Hollow, mostly perfectly round vugs with diameters from ~2 mm to 2 cm are present throughout the meteorite but appear to be more abundant in the porous part than in the compact shield rock. Most of them are empty, some are partly filled by carbonate and very few are filled by glass. They typically consist of a compact, fine- to medium-grained shell which is intergrown with the rock's matrix or borders to a druse (Fig. 2, see below). From now on we shall call these round vugs hollow shells.

#### 4.2. The Rock

The compact shield rock has a medium-grained micro-gabbroic texture with little pore space and scattered small open or closed druses and round hollow shells. Occasionally, some very thin (<1 mm) plagioclase + olivine plates (up to ~ 10 cm long!) are present. The transition into the porous lithology is gradual with the grain-size, pore-size and abundances of druses and hollow spheres increasing (Fig. 2).

The compact micro-gabbro-like rock consists mainly of an-

orthite, olivine and augite (Fig. 3). Anorthite forms large (up to > 2 mm long) hollow plates with highly complex cross sections. It is mostly intergrown with olivine, occasionally in a graphic way (Fig. 4). Such intergrowths can be enclosed by olivine or by large augite crystals. This way a subophitic texture is formed locally.

Beside olivine, anorthite occasionally also includes augite as well as a variety of other phases like spinel, magnetite, sulfides and a Fe-Ti silicate (see below).

#### 4.3. Olivine Megacrysts and Olivinite

Olivine is present throughout the rock and is usually intimately associated with anorthite, forming complex intergrowths, the round empty shells and large plates (see below). Throughout the rock large (up to 1 cm in diameter) olivine grains are present. They are more common in the porous part than the rest of D'Orbigny and come in three varieties:

1. Large green crystals, which are clear and transparent and have tracks of secondary fluid/mineral inclusions, commonly containing sulfides (Fig. 5). Their shapes range from equi-dimensional to platy or shard-like. These olivines are intimately intergrown with the host rock –no pore space is left. The most common overgrowths are anorthite-olivine intergrowths, less common augite.
2. Large polycrystalline olivinites consist of large, clear, green olivine grains of up to 8 mm in diameter or of milky greenish-white olivines. The shapes of these olivinites are very complex ranging from thin shards over irregular fragments to blocky fragments. The polycrystalline olivines are also intimately intergrown with the host rock and are also mostly accompanied by anorthite-olivine intergrowths, like the large single olivine grains. Olivinites in part also border to druses.
3. Milky greenish-white fragments of very fine-grained polycrystalline olivine. The fragments have the size of the iso-

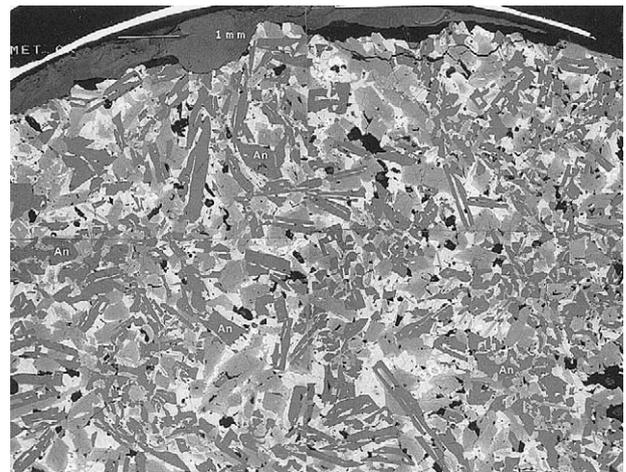


Fig. 3. Back scattered electron (BSE) image of D'Orbigny polished thin section (PTS) A. Different shades of gray are anorthite (An, dark), olivine, augite, Fe-augite, kirschsteinite (light), white are opaque phases (sulfides, oxides), black are holes. Note the complex hollow morphology of the anorthite visible in planes semiparallel to and cutting the elongated crystals which in many places form aggregates.

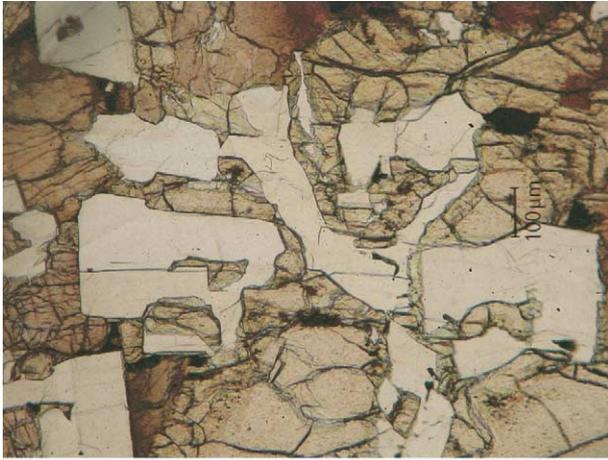


Fig. 4. Anorthite (white)-olivine (brown) intergrowth in transmitted light (A). Both phases are intimately intergrown, olivine is in places replaced by augite (dark brown). (B) Same as (A) but under crossed polarizers. Olivine has mostly the same optical orientation (consists of a single crystal) and anorthite forms many twinned individual grains.

lated clear olivines and consist of very fine-grained intergrowth of olivine that give a powder line X-ray diffraction pattern when placed into the single crystal CCD diffractom-

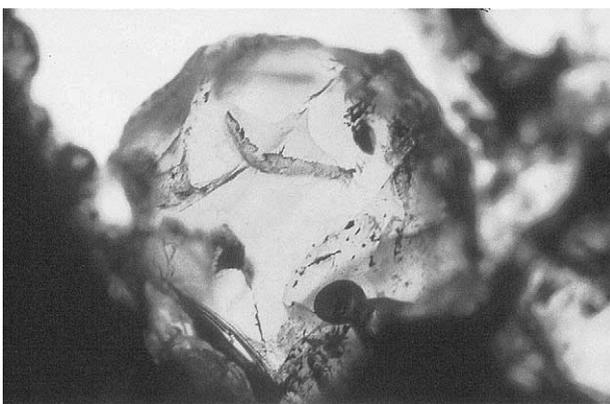


Fig. 5. Olivine megacryst (~ 7 mm) in the D'Orbigny angrite. The grain is transparent, green and contains only a few trails of secondary mineral ± fluid inclusions.

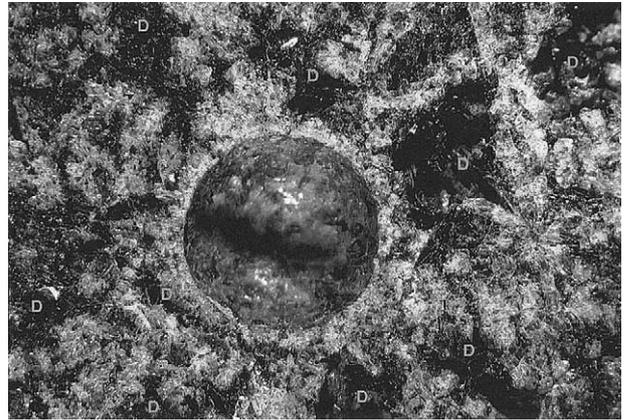


Fig. 6. Hollow shell consisting of fine-grained anorthite-olivine intergrowths with protrusions perpendicular to the shell's surface on freshly broken surface of D'Orbigny. Note the fractal character of the arrangement of anorthite-olivine intergrowths. The shell also borders to augite-rich lithology (left) and to druses (D) at upper and lower right side. Width of picture is 18 mm.

eter. The style of intergrowth appears to be that of milky fine-grained quartz veins from the terrestrial crust.

#### 4.4. Hollow Shells

Hollow spherical shells (hollow lithophysae or stone balls) are unevenly distributed throughout D'Orbigny, present in all parts, but are most common in the porous inner portion (Figs. 1, 2, 6). They are between a few mm and 2.5 cm in diameter, only very few with apparent diameters of < 200 μm have been encountered in thin sections. The shell is a compact granular intergrowth of fine-grained anorthite and olivine with occasionally some augite at the outside (Figs. 6 and 7). The grains in the shells have a tendency to be oriented perpendicular to the surface. The inner side of the shells is fairly smooth but has a roughness suggestive of replicating a former solid filling with granular texture (shell fills former indentations at grain boundaries, see Fig. 7). The inner surface is commonly lined with a

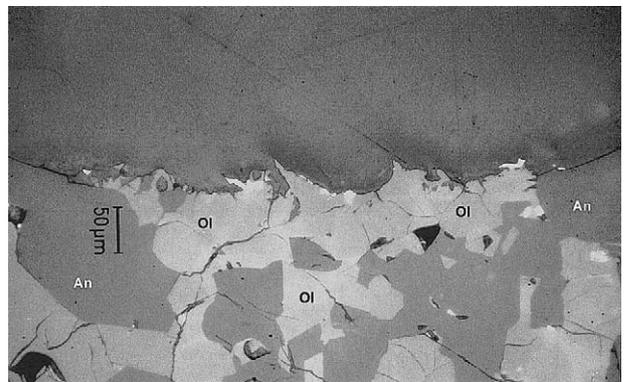


Fig. 7. Detail of a hollow shell's inner surface. Shell minerals—olivine (Ol, gray), anorthite (An, dark gray)—replicate the former surface on which they were deposited. There were grain boundaries with open wedges which were filled by the mineral deposited on top. Note the abundance of sulfides (white) which commonly line the inner side of shells. Reflected light picture.

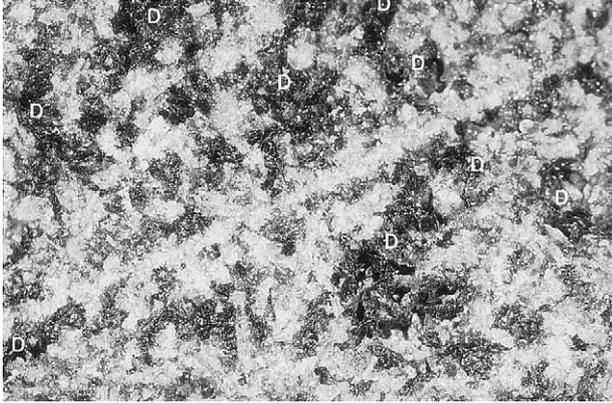


Fig. 8. Plate consisting of anorthite-olivine intergrowths (Figs. 4, 6). Note protrusions of anorthite-olivine intergrowths from the plate and druses on both sides. Dark is augite and black is pore space. Length of picture is about 2 cm.

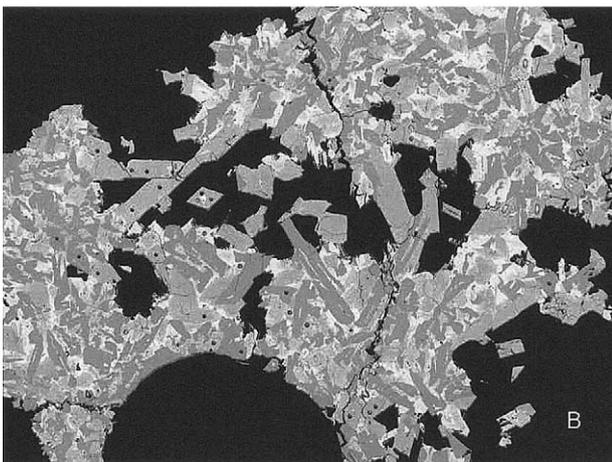


Fig. 9. (A) Black shiny augite crystals in open druse in D'Orbigny. Width of picture is 6 mm. (B) Polished section through a shell (bottom) and a small druse displaying euhedral augite and anorthite crystals protruding into the open space. Note also the high porosity outside the druse. Small dots are ablation holes from LA-ICP-MS analyses. BSE picture. Width of picture is 1 cm.

thin non-continuous cover of sulfides which occasionally forms geometric figures like parallelograms. A few large spheres have double-layered shells with a dark pyroxene-bearing layer between inner and outer olivine-rich layers. The overwhelming majority of shells are singles, only one double shell (two shells attached to each other) has been encountered and no multi-shell has been found.

#### 4.5. Anorthite-Olivine Plates

The dense and the fluffy parts of D'Orbigny contain occasionally large (up to 10 cm long) but thin ( $\sim 1$  mm) plates consisting of anorthite-olivine intergrowths like the ones forming the shells (Fig. 8). These plates can be straight or bent and have rough surfaces with abundant off-springs of short branches of intergrowths of anorthite and olivine. They are occasionally accompanied by short plates of the same composition either in a semiparallel or completely independent way.

#### 4.6. Druses

Druses are omnipresent in the porous portion of D'Orbigny (Figs. 1, 2, 6). They are irregular, open spaces up to  $> 3$  cm in elongation into which perfectly crystallized augites of prismatic habit and occasional anorthite plates protrude (Figs. 9, 10). Druses border to walls consisting of mainly anorthite-olivine intergrowths with low to high contents of augite. Small druses in the compact lithology of D'Orbigny commonly have only little void space and are almost closed. Druses are very commonly associated with hollow shells (Figs. 2, 6).

#### 4.7. Glasses

Glasses in the D'Orbigny angrite occur in the following modes: (a) glass filling in partly open druse space with free surfaces forming menisci, (b) glass filling a few of the abundant hollow shells, (c) glass pockets in olivine and (d) glass inclusions in olivine. The sizes of these glasses vary from tens of  $\mu\text{m}$

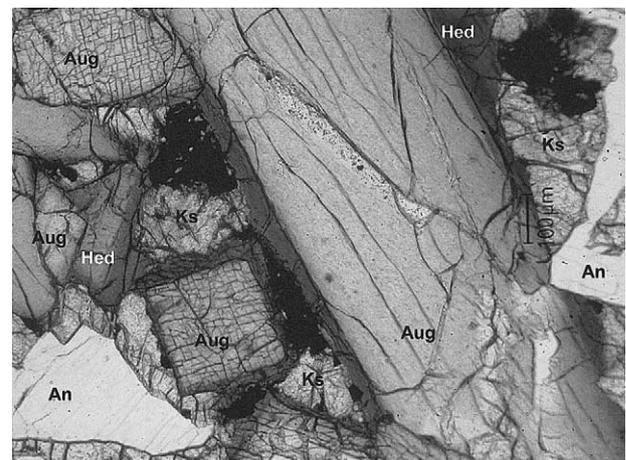


Fig. 10. Augites (Aug) in a closed druse in D'Orbigny. Note the asymmetrical overgrowths of titaniferous aluminous hedenbergite on augite (Hed, dark gray) and the filling of the wedges by titaniferous aluminous hedenbergite, kirschsteinite (Ks) and opaque phases (mainly sulfides). White grains are anorthite (An). Transmitted light picture.

Table 2. Selected electron microprobe analyses of oxide phases from angrite D'Orbigny (in wt%).

	OLIVINE				AUGITE				SPINEL						GLASS	
	groundmass				groundmass		druses		Al-rich						CC-1	
	mega	Core	rim	kirsch	core	rim	core	rim	PLAG	Ti-SILIC	Si-PHOS	ulvö	core	rim	reaction-rim	CC-1
SiO <sub>2</sub>	41.5	37.6	30.4	32.2	47.5	42.1	46.4	45.0	43.7	27.1	12.8	0.21	0.10	0.05	1.11	40.8
TiO <sub>2</sub>	<0.02	<0.02	0.15	0.02	1.19	4.6	1.53	1.91	<0.02	8.0	1.73	26.7	0.22	0.33	1.53	0.86
Al <sub>2</sub> O <sub>3</sub>	0.13	0.09	0.04	0.05	7.6	4.3	8.1	9.4	34.7	12.3	0.23	3.1	58.1	57.9	42.8	13.3
Cr <sub>2</sub> O <sub>3</sub>	0.29	<0.02	0.12	0.04	0.10	0.21	0.21	0.19	<0.02	0.02	<0.02	0.06	7.7	7.5	15.1	0.11
FeO	9.1	31.2	57.1	48.1	12.6	26.8	12.7	13.0	0.76	40.5	5.0	67.5	21.6	22.7	30.9	23.3
MnO	0.10	0.34	0.85	0.75	0.21	0.28	0.20	0.17	<0.02	0.34	0.06	0.35	<0.02	<0.02	0.04	0.27
MgO	49.2	31.8	0.53	0.64	8.8	0.07	9.1	8.3	0.27	0.70	<0.02	<0.02	14.1	13.1	8.0	7.7
CaO	0.29	0.85	10.4	19.0	23.2	22.2	22.7	22.9	20.3	12.7	48.4	0.32	<0.02	<0.02	0.74	14.3
TOTAL	100.61	101.88	99.59	100.80	101.20	100.56	100.94	100.87	99.73	101.66	98.92*	98.24	101.82	101.58	100.22	100.66
X <sub>Mg</sub>	90.2	63.7	1.3	1.6	27.0	0.2	28.0	25.8								
X <sub>Fe</sub>	9.4	35.1	80.0	65.5	21.6	48.4	21.9	22.7								
X <sub>Ca</sub>	0.4	1.2	18.7	33.0	51.3	51.4	50.1	51.5								

mega: megacryst.

kirsch: kirschsteinite.

plag: plagioclase.

Ti-silic: Ti silicate.

Si-phos: Si phosphate.

ulvö: ulvöspinel.

\* includes 30.7 wt% P<sub>2</sub>O<sub>5</sub>

(glass inclusions) to several millimeters (in druses and shells). The most common glass fills former open spaces and is black (brown in transmitted light) with brilliant luster and conchoidal fractures. Glass occasionally contains only a few bubbles but can also be foamy, with all possible transitions, even over short distances. Some glasses show dark-light schlieren in transmitted light, which resemble flow lines. However, the associated bubbles are always perfectly round. Glasses occasionally contain rounded mineral and—rare—rock particles, some contain small dendrites of olivine and/or magnetite. Small (1–50 μm) sulfide blebs (Ni-bearing FeS) associated with small bubbles are common. An X-ray test of a representative sample of druse-filling glass revealed glass fringes only.

Primary glass inclusions hosted by olivine have sizes up to 20 μm and consist of glass and a shrinkage bubble with one of them containing a sulfide globule (Ni-free). The glasses are subject of a separate report (Varela et al., 2003a, 2003b).

#### 4.8. Mineralogy and Phase Compositions

The major minerals are olivine, anorthite and augite. Olivine in the rock and the shells always contains Ca and consists of a core of composition Fa<sub>35</sub>La<sub>1</sub> which is covered by a zone consisting dominantly of Ca-rich olivine (Fa<sub>80</sub>La<sub>19</sub>) which is covered by a zone consisting dominantly of kirschsteinite (Fa<sub>66</sub>La<sub>33</sub>). Both zones are composed of intimate intergrowths of these two phases but are separated by steep compositional gradients (Table 2, Fig. 11). The centers of olivines commonly display euhedral rhombic shapes with Ca-rich olivine and kirschsteinite intergrowths filling the intergranular space. Olivine megacrysts and olivines in olivinites have Fa<sub>9–11</sub>, are CaO-poor (~ 0.4 wt.%) and have thin rims of Ca-rich olivine and kirschsteinite at the contact with the host rock. Anorthite in the rock and in the druses is pure anorthite with minor contents of FeO and MgO but no detectible Na<sub>2</sub>O. Augites in the rock are

mostly of composition En<sub>27</sub>Fs<sub>22</sub>Wo<sub>51</sub> and are titaniferous and aluminous. They are overgrown by titaniferous aluminous hedenbergite (En<sub>0.2</sub>Fs<sub>48</sub>Wo<sub>51</sub>) which also fills most of the intergranular space (Fig. 10). The compositional grading towards the rim composition is steep and abrupt in sections perpendicular to the crystal faces—like the zoning in olivine. The augite of the druses has a composition very similar to that of the rock-forming augites' cores. A thin rim is visible in druse augites in thin section which is only slightly richer in Ti and Fe than the core.

Among the minor phases, Al-rich spinels are common and



Fig. 11. Anorthite (red), olivine (green) and augite (dark green). The olivine (center) has a rhombic habit and is chemically zoned from center to edge (shades of green) and overgrown by Ca-rich olivine (yellow) and kirschsteinite (ocher). Note that Ca-rich olivine and kirschsteinite are not forming simple consecutive rims but rather are intergrown with each other in a complex way. Bright yellow is ulvöspinel, white are sulfides and black are holes. False color BSE image.

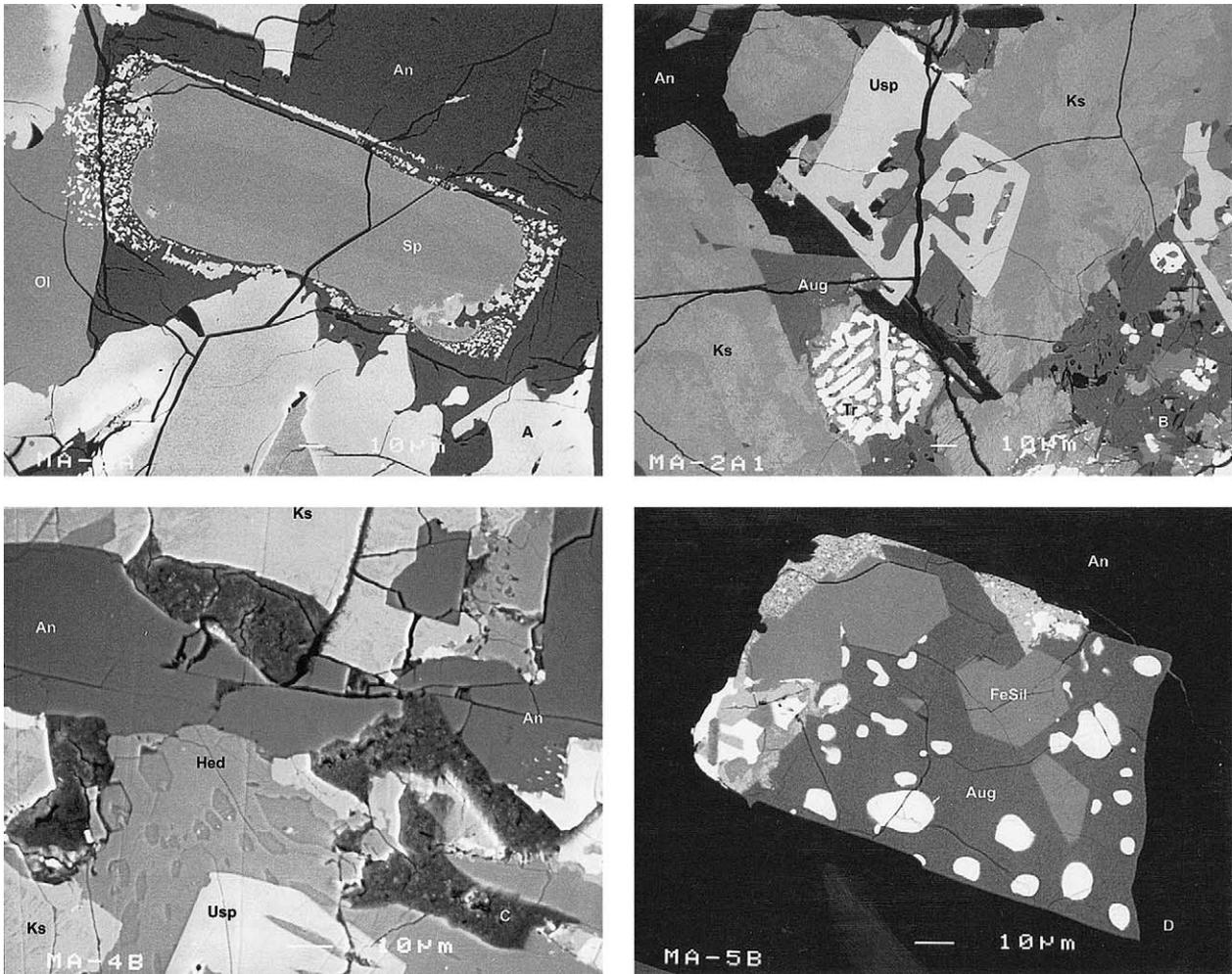


Fig. 12. BSE images of minor phases in D'Orbigny polished sections. (A) Al-spinel (Sp,  $\text{Cr}_2\text{O}_3 = 7.5$  wt.%, center, gray) enclosed by anorthite (An, dark) and olivine (Ol) and surrounded by a reaction zone consisting of spinel ( $\text{Cr}_2\text{O}_3 = 15$  wt.%) and anorthite and olivine (left). The large grain is compositionally slightly inhomogeneous. Bright gray is mainly kirschsteinite. (B) Skeletal ulvöspinel (Usp, center, gray) with kirschsteinite – Ca olivine intergrowths (Ks, mottled gray), anorthite (An, black), augite (Aug, dark gray) and silico-phosphate (in center of ulvöspinel, also dark gray) and a structured intergrowth of troilite (Tr) and kirschsteinite. (C) Titaniferous aluminous hedenbergite (Hed) containing euhedral crystals of silico-phosphate (lower center, all gray). At center lower edge is an ulvöspinel (Usp, light gray) to the left is kirschsteinite (Ks) and in the center is an anorthite (An, dark gray). Dark mottled areas are open space. (D) Multiphase inclusion in anorthite (An, black) consisting mainly of augite (Aug, dark gray) which contains euhedral crystals of a Fe-Al-Ti silicate (FeSil, gray), round blebs of magnetite and intergrowths of kirschsteinite and troilite.

typically associated with olivine and plagioclase (euhedral octahedra) and occur as large, anhedral grains. Spinel is Cr-bearing (about 7.5–11 wt.%  $\text{Cr}_2\text{O}_3$ ) and homogeneous in composition, except for the large spinels which are compositionally inhomogeneous and surrounded by a reaction zone (Fig. 12A) which contains spinel that is richer in  $\text{Cr}_2\text{O}_3$  than the large grain (about 15 wt.%  $\text{Cr}_2\text{O}_3$ ). Ulvöspinel is also common and occur typically in distorted skeletal crystals which are associated with anorthite, augite, olivine (also kirschsteinite), sulfides and occasionally also silico-phosphate (Fig. 12B). The ulvöspinel contains Al and Mn. The silico-phosphate contains Ti, is widespread and associated either with sulfides, kirschsteinite and ulvöspinel or occurs as euhedral inclusions in titaniferous and aluminous hedenbergite (Fig. 12C). An unknown Fe-Al-Ti-silicate was found in multi-phase inclusions in anorthite (Fig. 12D). The phase forms euhedral crystals of up to 20  $\mu\text{m}$

diameter, is enclosed by augite and associated with magnetite, troilite and kirschsteinite.

Troilite (Table 3) is very common and forms unusual inter-

Table 3. Selected electron microprobe analyses of non-oxide phases from angrite D'Orbigny (in wt%).

	Taenite	FeS	Ni-Pyrr.	Pentl.	Pentl.
Fe	61.2	63.0	62.0	46.6	42.4
Ni	38.9	<0.02	1.0	21.3	24.2
Co	0.92	<0.02	0.08	0.27	0.32
S	<0.02	36.2	36.4	33.4	34.0
TOTAL	101.02	99.2	99.48	101.57	100.92

Ni-Pyrr.: Ni-pyrrhotite.  
Pentl.: pentlandite.

Table 4. Trace element contents of D'Orbigny and other angrites (in ppm).

	D'Orbigny (1)	error %	AdoR #2 (2)	LEW 86010 (2)	LEW 87051 (2)	Asuka 881371(2)
Na	140	5	223	227	223	160
Ca	85000	15	162000	125000	86000	73000
Ti	4600	15	11800	9600	5100	
Sc	36	3	51	55	42	32.9
Cr	300	5	1490	890	1100	950
Mn	1600	10	990	1690	1890	1790
Fe	178000	5	80200	157000	163000	171000
Co	33	5	15.7	24.6	28.5	51
Ni	28	20	40	39	45	114
Ga	0.37	20	0.27	0.34		0.26
Sr	120	20	117	60	92	
Zr	50	15	102	51		34
Sb	0.03	30	0.097		0.145	
Ba	42	15	30*	51		
La	2.8	8	6.8	4.66	3.51	2.34
Ce	8	8	18.7	10.9	9.4	5.9
Nd	6	20	16.9	8.1	5.9	4.4
Sm	1.7	5	5.7	2.6	2.01	1.39
Eu	0.63	10	1.9	0.97	0.8	0.53
Gd	2.3	15				
Tb	0.35	8	1.32	0.61	0.49	0.33
Dy	2	30	8.6	4.4	3.2	2.3
Ho	0.5	5				
Er	1.7	30				
Tm	0.3	30				
Yb	1.5	5	4.9	2.61	2	1.38
Lu	0.23	15	0.72	0.38	0.3	0.21
Hf	1.2	8	2.43	1.87	1.34	1.03
Ta	0.15	30	0.37	0.29	0.15	
Ir	<0.001		0.00007	0.0071	0.00018	0.0024
Au	0.0008	15	0.005*	0.00037		
Th	0.33	8	0.55	0.4	0.41	0.24
U	0.08	20	0.11	0.15		

AdoR = Angra dos Reis.

(1) = this work.

(2) = Warren et al., (1995).

\* from AdoR #1

growths with olivine/kirschsteinite (Fig. 12B, D), globules in augite or glass, euhedral grains in augite and is part of multi-phase inclusions in augite, anorthite and glass. Pentlandite and Ni-bearing pyrrhotite (Table 3) commonly occur together and are associated with titaniferous aluminous hedenbergite. Metal is scarce, usually small, associated with sulfides and is of awaruite (FeNi<sub>2</sub>) composition.

The composition of the most common glass filling pore space is ultrabasic (see glass CC-1 in Table 2) and varies somewhat: SiO<sub>2</sub> (37 to 41 wt.%); TiO<sub>2</sub> (0.5 to 0.9 wt.%); Al<sub>2</sub>O<sub>3</sub> (11.9 to 13.3 wt.%); MgO (6.6 to 8.0 wt.%); FeO (23 to 26 wt.%).

#### 4.9. Major and Trace Element Abundances

The sample used for bulk analysis was cut from D'Orbigny by the owner and provided for identification. It was taken from the dense lithology of the upper shield, the front shield (Fig. 1A).

The bulk trace element contents as determined by INAA are given in Table 4. D'Orbigny is rich in refractory lithophile elements which have unfractionated relative abundances (about 10 × CI, Fig. 13A), except for Sc which is depleted with respect to the other refractory elements. Abundances of volatile

lithophile elements are low, Na < 0.1 × CI, Cr ~ 0.1 × CI, but Mn abundance is about chondritic. Abundances of siderophile elements (Fig. 13B) are also low, Ir < 0.002 × CI, Ni, Au < 0.01 × CI and Co, Ga < 0.1 × CI. The Fe abundance is high (~ CI abundance) as is the abundance of Sb (>0.1 × CI).

#### 4.10. Noble Gas Contents and Isotopic Composition

The concentration and isotopic composition of noble gases were measured in a bulk sample of 103.4 mg from the front shield dense lithology (Fig. 1A). The results are given in Table 5. The mean exposure age is 11.0 ± 0.8 Ma.

#### 4.11. Oxygen Isotope Composition

The oxygen isotopic composition of the bulk dense lithology of the front shield (Fig. 1A) is: δ<sup>18</sup>O = +3.5 ± 0.1, δ<sup>17</sup>O = +1.6 ± 0.1 ‰, Δ<sup>17</sup>O = -0.21 ± 0.10.

## 5. DISCUSSION

The genesis of angrites is a longstanding enigmatic subject. Before expanding on our new model, we will in Sec. 5.2 first briefly summarize the general knowledge on angrites and the

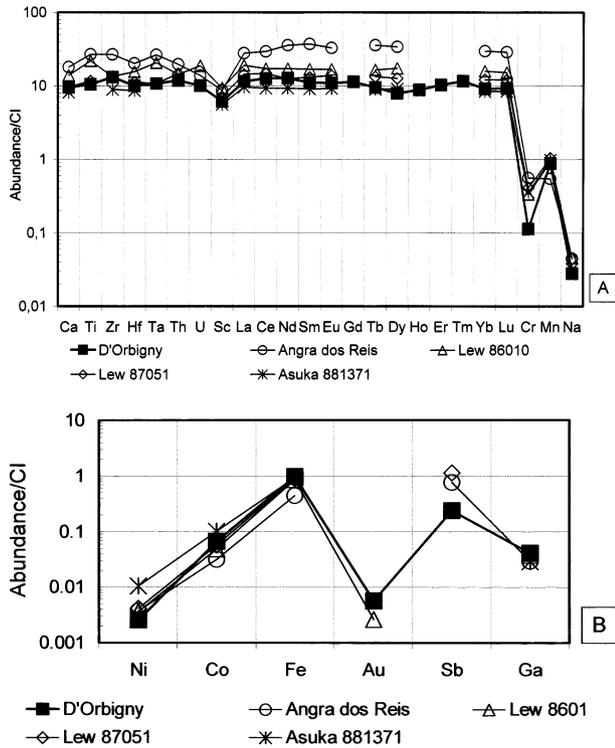


Fig. 13. CI-normalized (Anders and Grevesse, 1989) abundances of major and trace elements in D'Orbigny and in other angrites. (a) lithophile elements; (b) siderophile elements. Elements are arranged in order of increasing volatility, except for the REE which are arranged in order of increasing Z. Note the unfractionated relative abundances of the refractory lithophile elements (except Sc), the strong depletion in volatile and siderophile elements and the chondritic abundances of Fe and Mn.

existing (“canonical”) models and beliefs regarding their genesis including their shortcomings. From that we will proceed to discuss several key features of D'Orbigny with the aim to extract the genetic message from each of them (Section 5.3). Based on our conclusions we will try to draft a genetic model that can accommodate as many observations as possible: a new, simple way to create angrites will be proposed (Section 6).

**5.1. Classification of D'Orbigny**

All data acquired on D'Orbigny fit its classification as an angrite (Table 1). Thus, D'Orbigny is the sixth angrite known and it is by far the most massive one. Maybe because of its size we were able to see and study overall structures not observed before in any other angrite. Most parts of the meteorite textur-

ally and mineralogically resemble angrites described previously, like Asuka 881371 and Sahara 99555 (Yanai, 1994; Prinz and Weisberg, 1995; Warren and Davis, 1995; Bischoff et al., 2000; Mittlefehldt et al., 2002). Also, the mineral compositions are very similar to those of previously described angrites (see below). The oxygen isotopic composition with  $\Delta^{17}\text{O} = -0.21 \pm 0.10$  is within the range of all other angrites,  $\Delta^{17}\text{O} = -0.16 \pm 0.05$  which places D'Orbigny clearly into the angrite/HED field (Clayton and Mayeda, 1996). However,  $\delta^{17}\text{O}$  with  $+1.6 \pm 0.1$  ‰ extends the range observed so far ( $\delta^{17}\text{O} = +1.74$ – $+1.94$  ‰).

The noble gases observed in D'Orbigny (Table 5) are very similar to those found in other angrites and are characterized by high amounts of radiogenic  $^4\text{He}$ , due to the relatively high U concentrations, and low  $^{40}\text{Ar}$  caused by very low K concentrations. We did measure  $120 \pm 8$  ppm K in our sample but this must mainly be due to terrestrial contamination and is, therefore, not given in Table 4. Taking the Na content of  $140 \pm 5$  ppm as an upper limit, the corresponding (chondritic) K content could be  $\sim 14$  ppm. Because in meteorite finds with low indigenous contents also Ar is prone to terrestrial (atmospheric in this case) contamination, the calculation of a K-Ar age is impossible. The U/Th- $^4\text{He}$  gas retention age is 4.55 Ga and the Pb-Pb age is  $4.559 \pm 0.0011$  Ga (Jagoutz et al., 2002a). This demonstrates that D'Orbigny is very old and was not involved in a major thermal event since its origin.

Exposure ages are calculated from cosmogenic  $^3\text{He}$ ,  $^{21}\text{Ne}$  and  $^{38}\text{Ar}$  using production rates calculated from the chemical composition of the angrite Sahara 99555 (Bischoff et al., 2000). The ages calculated from these three nuclides agree very well and result in a mean exposure age of  $11.0 \pm 0.8$  Ma, which is different from that of other angrites: Angra dos Reis—55.5 Ma; LEW 86010—17.6 Ma; Asuka 881371—5.3 Ma; LEW 87051— $\geq 0.2$  Ma; Sahara 99555—6.1 Ma (see Eugster and Weigel, 1995; Bischoff et al., 2000). D'Orbigny thus represents a sample from an independent meteoroid-producing event on the angrite parent body.

**5.2. The Canonical Model: Angrites as Igneous Rocks**

In the canonical model, angrites are widely believed to be igneous rocks of basaltic composition originating from a differentiated planetesimal (e.g., Treiman, 1989; Mittlefehldt and Lindstrom, 1990; Longhi, 1999; Mittlefehldt et al., 2002). Beside the basaltic angrites there is also Angra dos Reis (Table 1), which is considered the “augite cumulate rock” of the angrite family and either a cumulate from an angritic melt (e.g., Prinz et al., 1977) or the product of crystallization of a melt of its own chemical composition (Treiman, 1989; Mittlefehldt and

Table 5. Rare gas (He, Ne, Ar) isotope abundances and exposure age of bulk D'Orbigny (103.4 mg).

Sample	$^3\text{He}$	$^4\text{He}$	$^{20}\text{Ne}$	$^{21}\text{Ne}$	$^{22}\text{Ne}$	$^{36}\text{Ar}$	$^{38}\text{Ar}$	$^{40}\text{Ar}$
D'Orbigny	17.3	14200	2.28	2.31	2.62	1.36	1.99	50
	$t_3$	$t_{21}$	$t_{38}$	t(mean)				
	10.6	11.9	10.4	$11.0 \pm 0.8$				
		[Ma]						

Lindstrom, 1990; Longhi, 1999), which has a much higher trace element content than the possible parent melts for the basaltic angrites (e.g., Treiman, 1989; Mittlefehldt et al., 1998). Thus, two principally different basaltic liquids are necessary to create the angrite family, possibly more.

In the model, the source of angritic liquids remains unknown. Melts chemically resembling those of bulk angrites have been successfully produced by partial melting of carbonaceous chondrites (C chondrites) under oxidizing conditions (Jurewicz et al., 1993). Very high oxygen fugacity conditions (IW+2) during partial melting of Allende were found to produce the necessary highly silica-undersaturated liquids. None of the experimentally produced liquids, however, matches angritic liquids in all parameters.

### 5.2.1. Textural and experimental evidence for an igneous origin

Textural evidence for an igneous origin is provided by the subophitic to variolitic textures of most basaltic angrites, which are suggestive of formation from a liquid (e.g., LEW 87051, Asuka 881371, Sahara 99555). In particular, variolitic textures of Asuka 881371 and LEW 87051 give evidence for crystallization from an under-cooled melt. The abundant presence of glasses in D'Orbigny with a composition similar to that of Asuka 881371 melt rock portion (Prinz and Weisberg, 1995) and to YA 1154 (a small angritic rock fragment described by Yanai, 2000) provide also evidence for the existence of angritic melts. Apparently, in most cases they were chilled to fine-grained rocks and possibly formed some of the coarse-grained doleritic angrites. Only in very rare cases they were chilled to glass.

The basaltic angrites (consisting of anorthite, olivine and augite) can be modeled to have crystallized from a melt with a composition of that of the bulk rock (e.g., McKay et al., 1994; Longhi, 1999). Melting experiments performed by McKay et al. (1988) on a composition similar to that of LEW 86010 successfully reproduced the pyroxene compositions of and a rock similar to LEW 86010. Also, Mikouchi et al. (2000a) successfully reproduced the groundmass of Asuka 881371.

### 5.2.2. Problems with the igneous model

None of the angrites appears to have formed from a multi-phase saturated liquid as would be expected for a liquid produced by partial melting of an ultramafic chondritic source. Textures commonly suggest olivine to be the liquidus phase. Eliminating these olivines by classifying them as xenocrysts puts anorthite onto the liquidus. The crystallization sequences for angrites can be deduced from their textures but are model-dependent, i.e., if the olivine and spinel megacrysts are indeed xenocrysts (Prinz and Weisberg, 1995; Prinz et al., 1990; Mikouchi et al., 1996; Mittlefehldt et al., 1998, 2001) then the crystallization sequence deduced from texture is anorthite + olivine followed by anorthite + olivine + augite followed by anorthite + olivine + augite + ulvöspinel. Modeling crystallization of D'Orbigny from its bulk chemical composition (Kurat et al., 2001c) following the procedure of Ariskin et al. (1997), however, does not support this sequence of crystallization: anorthite is the liquidus phase and crystallization proceeds

(after 7% of melt crystallized) with anorthite + olivine, followed (after > 50% of melt crystallized) by anorthite + olivine + augite. Such a sequence is only shown by LEW 86010 (Delaney and Sutton, 1988) which has abundant large anorthite grains set into a granular matrix. However, basaltic angrite LEW 86010, which is the by far best investigated angrite so far, has an unequilibrated granoblastic texture which is very far from any possible igneous texture and rather resembles a metasomatic replacement texture (see pictures in Mittlefehldt et al., 1998; Mikouchi et al., 2000b). Nevertheless, this rock is also believed to be of igneous origin.

In addition, the highly oxidizing conditions necessary for angrite melt formation from C chondrites should produce Ni, Co, W-rich silicate melts, which is clearly not the case. The siderophile elements, refractory or non-refractory, are all missing and testify for an early siderophile—lithophile element separation (Jones et al., 1988). The highly variable Fe/Mg ratios of angrites cannot be accommodated by such a melt formation (see Prinz and Weisberg, 1995; Mittlefehldt et al., 1998). Furthermore, there is no proper explanation for the lack of alkalis in angrites because there is no alkali-free chondrite. Distilling small amounts of melts was suggested (Prinz and Weisberg, 1995) but as evaporation will be diffusion-controlled, such a process can explain alkali deficits in some small calcium-aluminum-rich inclusions (CAIs) but we do not see how it can be efficient enough to explain the very low alkali abundances in angrites.

Furthermore, Angra dos Reis, the “augite cumulate rock” of the angrite family, consists overwhelmingly of augite and is highly deficient in co-crystallizing olivine and anorthite. Obviously, there cannot be just one parental bulk chemical composition for all angrites. Furthermore, Angra dos Reis cannot be directly related to the basaltic angrites because it is about two times richer in trace elements than the latter. Pyroxene cumulates from basaltic liquids should be depleted in trace elements as compared to the liquid from which they formed. A possible formation of Angra dos Reis from an evolved angritic liquid after precipitation of anorthite and olivine (i.e., after > 50% crystallization), which will about double the trace element content of the remaining liquid, is unlikely, as co-precipitating olivine and anorthite are missing—as outlined above. This will also not be enough to produce the very high trace element contents in Angra dos Reis augite (Croaz and McKay, 1990) and it will produce a negative Eu anomaly in the liquid that should be visible in the REE pattern of the augite, which is not the case. Furthermore, the distinct negative abundance anomaly for Sc exhibited by Angra dos Reis should not exist because pyroxene is the favorite site for Sc in basaltic rocks (see distribution coefficients in Green, 1994).

Treiman (1989) showed that Angra dos Reis could have formed from a melt with the composition of the whole rock. The problem is that this melt is not saturated in olivine and that it produces only pyroxene but no olivine (which is present in appreciable amounts in Angra dos Reis).

All experiments done on basaltic angritic compositions created approximate counterparts of angrites but none of them succeeded in fully creating any known angrite. The melting experiments of McKay et al. (1988) on compositions similar to that of LEW 86010 showed that this angrite could have formed from such a melt but were unable to reproduce the modal

composition of LEW 86010, which contains excessive olivine and anorthite with respect to the experimental product. Mikouchi et al. (2000a) experimented with melt compositions similar to that of Asuka 881371 groundmass under IW+2 redox conditions and variable cooling rates. In most of their runs they were not able to reproduce the groundmass mineral assemblage olivine(39%) + anorthite(36%) + augite(20%) (mode from Yanai, 1994). Although olivine and augite were present in all their runs, anorthite was present only in a few. However, they report no modes for their experimental products, so comparison with the real angrites is not possible.

The widely used textural argument in favor of the igneous model holds for the obviously chilled melts such as Asuka 881371 and LEW 87051 but is not applicable to all ophitic and subophitic textures, which give evidence for co-crystallization of olivine + anorthite and olivine + anorthite + augite only but usually do not give any information on the medium from which the crystals grew. It is commonly assumed—also for the terrestrial counterparts, dolerites—that crystallization occurred from a melt. Common pore space and inclusions of chilled melts in terrestrial dolerites indicate formation from a volatile-rich melt or melt-bearing fluid—as it is likely the case also for D'Orbigny.

### 5.2.3. Non-fitting reality

Many conflicts between an igneous model for the origin of angrites and mineralogical and chemical observations as in part discussed above have been noticed previously (see, e.g., Prinz et al., 1977, 1988; McKay et al., 1988; Treiman, 1989; Jurwicz et al., 1993; Prinz and Weisberg, 1995; Longhi, 1999; Mittlefehldt et al., 2002) but did not lead to a revision of the model. Beside mineralogical and geochemical problems, there is the impressive antiquity of angrites which is manifested by the presence, during their formation, of short-lived radio-isotopes, such as  $^{53}\text{Mn}$  (Nyquist et al., 1994, 2003),  $^{146}\text{Sm}$  (Lugmair and Marti, 1977),  $^{244}\text{Pu}$  (Hohenberg, 1970; Lugmair and Marti, 1977; Eugster et al., 1991),  $^{182}\text{Hf}$  (Quitté et al., 2000) and possibly also  $^{247}\text{Cm}$  (Jagoutz et al., 2003). There is the presence of trapped Xe-Q, a very primitive, chondritic Xe component (Busemann and Eugster, 2002) which cannot be expected to be preserved in silicate melts. All these features point towards a possible primitive origin of angrites, an origin comparable to that of other achondrites (e.g., Kurat, 1988, 1990).

The question of the source of angritic melts creates fundamental problems for any partial melting model as the high refractory trace element (RTE) abundances require a low degree of partial melting of a chondritic source but relative abundances (that are approximately chondritic) require a high degree of melting as does the unfractionated Eu content: the residuum should not contain any trace element carrier (pyroxene) and no feldspar. One way out of this crisis is to enrich the source in CAIs before melting, as proposed by Prinz et al. (1988, 1990) and Prinz and Weisberg (1995) but this requires the principal elemental fractionations to take place in the solar nebula, thus having primitive roots. However, it does not solve the alkali problem as the source needs to not only be enriched in CAIs but also be devoid of alkalis. Such meteorites are not known so far.

Another problem is posed by the siderophile elements, which are present in angrites in only very low amounts. A silicate liquid created under IW+2 redox conditions should carry large amounts of  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ , but the former is present in very low amounts only and the latter is almost completely missing. Instead, Ni-bearing metal and sulfides are present in angrites (e.g., Prinz et al., 1977, 1988, 1990; Prinz and Weisberg, 1995)—also in D'Orbigny (see below).

Longhi (1999) investigated the problem of parent melts for angrites in detail and concluded: “No single group of meteorites  $\pm$  Fe simultaneously satisfies the constraints of Mg' and silica component”—both necessary for the creation of angritic liquids. He finally states that “. . . the low-silica component was not simply an enrichment of CAIs, but was the result of direct accretion of high-temperature condensate (Grossman, 1972) into sizeable, thermally shielded planetesimals. Thus angrites cryptically record mixing of planetesimal-sized heterogeneities in the early solar system.” This comes close to what we are going to conclude but the necessity of a planetesimal-sized parent body is born solely out of the deep-rooted belief by the author that angrites are planetary igneous rocks.

Obviously, alternative possible ways to the igneous planetesimal formation model for angrites need to be explored (e.g., Kurat, 1988, 1990). As discussed below, the need is strongly enforced by our new observations on D'Orbigny.

## 5.3. The Case of D'Orbigny

### 5.3.1. Shape and structure

The peculiar shape of D'Orbigny (Fig. 1) appears to be a consequence of its structure. The ablative mass loss must have been low, otherwise the pan-like back side could not have survived. As this pan shape cannot be of atmospheric origin, it must reflect a preatmospheric feature of the D'Orbigny meteoroid. If the back pan survived at large, the front shield might have as well. Consequently, we can assume that the two shields were only partially modified during atmospheric entry and grossly reflect the preatmospheric shape of D'Orbigny. The porous lithology situated in between the two shields must have lost substantial amounts of its mass, presumably during atmospheric entry as well as afterwards. This is evidenced by the lack of fusion crust and the presence of deep scars from a plow. The physically unstable porous lithology has doubtlessly also de-stabilized part of the front shield and from the morphology of the front shield edge we deduce that some portions, amounting to 10–20% of the final shield area, were lost by break-off early and late during atmospheric entry. Nevertheless, most of the shield matter apparently survived with only flat regmaglypts having been burned into it.

We can conclude that the shape of D'Orbigny is indeed a consequence of its internal structure. In our view, this structure cannot be reconciled with an igneous origin of the rock because such a mushroom-like shape needs directional growth in free space with repetitively changing conditions. If grown in a melt, such a shape cannot be recovered without melt (i.e., later crystallized rock matrix) at least in part attached to it and, especially, filling the back pan. Then, the latter will have to be carved out of the solid rock.

### 5.3.2. The building blocks

The subunits of which D'Orbigny has been made of are: the hollow shells, the olivine megacrysts, the anorthite-olivine intergrowths, the open voids and druses and the augite. This will be discussed in detail in the following.

#### *The Shells*

The hollow shells are made almost exclusively of an intimate intergrowth of anorthite and olivine (Figs. 2, 6, 7, 9A), with minor Cr-bearing Al-spinel. The shells apparently were formed by precipitation onto a solid sphere that happened to have a sculptured surface which was replicated by the precipitate (Fig. 7). From the morphology of the inner side of the hollow shells we can deduce that the solid constituting the spheres had a smooth surface with a few wedges. This could indicate either a granular or a concentric fibrous texture with a botryoidal surface. The fact that this solid does not exist anymore, is evidence for it becoming unstable in the course of the evolution of the rock. Because the late stages of the formation of D'Orbigny and the other angrites are characterized by strongly oxidizing conditions (see Brett et al., 1977), the solid(s) previously present in the spherical shells could have been a reduced phase or phases unstable under oxidizing conditions. As this phase(s) vanished during oxidation it cannot have been a silicate but rather a phase that breaks down into volatile species (CaS? See below).

These shells are called “vesicles” by Mikouchi and McKay (2001) and Mittlefehldt et al. (2002), among others, and have been interpreted as representing bubbles in the melt. Comparison with bubbles in basaltic melts, however, reveals that such bubbles are usually lined by basalt—as they should be, and not—as in the case of D'Orbigny—by anorthite + olivine intergrowths. Terrestrial basalts to our knowledge do not show such a feature. While bubbles in lunar basalts can be preferentially covered by a single mineral or a combination of a few minerals (e.g., Schmitt et al., 1970), this is not the rule and the same mineral combination does not form other structures in the rock, such as in our case plates (Fig. 8) and a fluffy framework (Fig. 6). Also, such covers on bubbles in lunar basalts may have crystals protruding into the vesicle but they do not have a surface that is replicating a preexisting surface. Hence, there is no similarity between the D'Orbigny shells and lunar basalt bubbles and therefore an igneous gas bubble origin of the former appears to be unlikely.

In summary, the hollow shells are very likely morphologic copies of possibly the earliest phase present and represent the second-oldest building unit of D'Orbigny. They are likely one of the oldest surviving major building units of the rock.

#### *Olivine megacrysts and olivinites*

The large olivine megacrysts (Fig. 5) and olivinites possibly are also one of the oldest surviving major building blocks of D'Orbigny. Their chemical composition is so far away from those of possible precipitates from angrite parent melts that in the igneous model they are usually considered “xenocrysts” (e.g., Prinz et al., 1990). They were likely collected together with the solid spheres and it is, therefore, likely that the unknown phase constituting the spheres stably co-existed with olivine. Megacryst olivine and olivinite are the most magnesian phases encountered in angrites (e.g., Prinz and Weisberg, 1995). However, their fayalite content of about 9 mol.% may

not be the original value, and the same is possibly true for some of the minor element contents (see below). In any case, these “xenocrysts” and “xenoliths” indicate more reducing conditions during their formation than is shown by the host rock.

Both olivine megacrysts and olivinites are tightly intergrown with the host rock—in many places via anorthite or olivine but also with augite. The border zone has steep compositional gradients between the Fo-rich core and Fa-rich overgrowths indicating alteration by a late-stage metasomatic event rather than magmatic compositional zoning. Mikouchi et al. (2001) recognized this border zone to be an overgrowth and were able to calculate a cooling rate ( $\sim 10$  °C/h between 1300 and 1000 °C) from the diffusion zone between the chemically homogeneous core and the Fe-rich overgrowth. Such a high cooling rate is in stark contrast to the grain sizes and the homogeneous chemical composition of large volumes of olivine and augite grains, which need slow growth conditions and ample time for chemical homogenization.

The nature of the very fine-grained polycrystalline olivine is enigmatic. It could be a secondary breakdown product of former well-crystallized olivines. Mikouchi and McKay (2001) suggest that this happened in a shock event. However, as there are no indications of shock in D'Orbigny, a thermal event seems to be more likely. But the fine-grained texture of polycrystalline olivine could also be a primary (precipitation) feature. Obviously, the answer to this question will have to wait until more data will be available.

The chemical composition of the olivine megacrysts is magnesian and they are rich in minor elements. They, therefore, very much resemble olivines from C chondrites (Hoinkes and Kurat, 1975; Kurat, 1975; Kurat and Kracher, 1980; Steele et al., 1985; Palme et al., 1986; Kurat et al., 1989a). This similarity also includes high trace element contents (Kurat et al., 1989b, 2001c; Crozaz and McKay, 1990; Weinbruch et al., 2000), the high Cr<sub>2</sub>O<sub>3</sub> content and the chondritic FeO/MnO ratio (Table 2). It is conceivable that these olivines had an evolution similar to olivines in C chondrites, i.e., they formed as Ca, Al-rich forsterites by condensation and were subsequently metasomatized which led to high FeO, MnO and Cr<sub>2</sub>O<sub>3</sub> contents and to a chondritic FeO/MnO ratio—a consequence of the chondritic reservoir (Kurat, 1988; Dohmen et al., 1998).

In summary, olivine megacrysts and olivinites appear to be early formed constituents of D'Orbigny. They likely formed under reducing conditions and probably were stable companions of the phase(s) constituting the solid spheres. They subsequently experienced Fe-Mn-Cr metasomatism fed from a chondritic source which established their final composition.

#### *Anorthite-olivine intergrowths*

Anorthite-olivine intergrowths are also a major constituent of the compact and fluffy lithologies of D'Orbigny (Figs. 2–4, 6). The rock can in fact be described as consisting mainly of a fluffy, highly porous aggregate of anorthite-olivine intergrowths with the pore space being either totally or partly filled by augite. This is particularly well documented in Figures 2 and 6. Anorthite-olivine intergrowths also form plates (Fig. 8, Kurat et al., 2003a), straight or curved, which are thin and can be very large ( $\sim 10$  cm) with respect to their thickness (0.2 –  $\sim 1$  mm). They are part of the fluffy network of anorthite-olivine intergrowths and probably had to grow undisturbed in free space.

Protrusions of the same composition from these plates link to the network that appears to form the backbone of the rock.

The shell shown in Figure 6 has developed radial extensions with abundant pore space within and in between the outgrowing anorthite-olivine units. The pore space is only partly filled by augite, most of it is open and contains shiny druse augites. Clearly, the anorthite-olivine intergrowths represent early precipitates and the augite a late phase (see also Fig. 4).

The anorthite-olivine intergrowths plates and networks are relatives of the shells and they probably formed contemporaneously with the shells. The anorthite-olivine co-precipitation seems to have been the major precipitation event that took place with the spherule-forming phase still alive, which means, that this precipitation likely took place under not yet strongly oxidizing conditions. Consequently, although  $\text{Fe}^{2+}$  was possibly already available—as evidenced by the spinel composition, see below—the olivines which formed in this event were likely not very rich in FeO, maybe comparable to the composition of olivine megacrysts.

In summary, the anorthite-olivine shells and the anorthite-olivine intergrowths could have formed contemporaneously by precipitation from a vapor phase and formed a loose and highly fluffy aggregate which later became the backbone of the rock. The shield lithologies were preset by small anorthite-olivine objects which aggregated early, allowing some of the pore space to be filled also by anorthite and olivine. The back side pan-like shield must be a negative replica of a preexisting convex or round object. We have no hint as to what this object might have been made of. On top of this shield material radially fingering aggregates of anorthite-olivine intergrowths set the stage for what later became the porous lithology.

#### *Druses*

All open space between the anorthite-olivine objects contains abundant shiny and perfectly crystallized augite crystals and occasionally also some anorthite (Figs. 2, 6, 8, 9). Obviously, the crystals grew into the void space and the most likely process for this—in analogy to terrestrial druses—is a pneumatolytic process. There is an obvious morphologic and chemical relationship between the druse augites and the large augites in the host rock. There can be no doubt that most of the latter were formed in a very similar way as evidenced by many closed or almost closed druse voids (Fig. 10) and by the chemical composition (Table 2). There is no difference in chemical composition between the druse augites and the large, homogeneous cores of the large augites in the rock, hence the same origin is indicated. Pneumatolytic growth of augites could have been fed by a decomposing Ca-rich phase ( $\text{CaS}$ ?) from the now empty shells during an oxidizing event. Growth apparently occurred where the reactants met: in interstitial void space, small and large. In part, also olivine appears to have reacted with a Ca, Al-rich vapor to form augite. Most augites must have formed this way as they have approximately the same and homogeneous chemical composition and are Al-rich and Ti-poor (cores of groundmass augites and druse augites—Table 2). Temperature likely was high and Mg was available.

One difference, however, exists between the augites in the rock and those in the druses. The former have titaniferous aluminous hedenbergite overgrowths or wedge fillings (Fig. 10). The druse crystals protruding into free space have no

compositional zoning but where they are seated at the druse wall, wedges are also filled by titaniferous aluminous hedenbergite (Fig. 9B). Apparently, this phase was deposited very late and only in places where the reactants (unknown) met or where a transport vehicle was available. Formation of this phase (and of the other phases of the late ferroan titaniferous phase assemblage) within tight pore space of the rock but not in the wide open druses indicates that at least one of the reactants must have come from inside the host rock and the other from outside. Clearly, such a feature is difficult, if not impossible, to establish by a fractionated melt which primarily should have reacted with and coated the freely accessible crystals protruding into the void space.

Also, in this case one of the reactants could have been a volatile phase produced by the decaying spherule-forming matter. Species like  $\text{Ca}(\text{OH})_2$  (from oldhamite,  $\text{CaS}$ ) and  $\text{Ti}(\text{OH})_4$  (from osbornite,  $\text{TiN}$ ) could have been involved. The associated Fe and Mn must have had a source with chondritic Fe/Mn abundance ratio. Very likely, this source was outside the rock.

In summary, the druses appear to be the product of pneumatolytic processes which became active after the fluffy aggregate network of shells plus anorthite-olivine intergrowths was formed. Part of the reactants could have come from the decaying spherule phase(s) which became unstable under strongly oxidizing conditions. The Fe-Mn component likely has been supplied by a chondritic source. Oxidation conditions must have been severe and proper amounts of  $\text{H}_2\text{O}$  were available to provide mobility for Ca and Ti (and other elements like REE; e.g., Hashimoto, 1992).

#### *5.3.3. Phase compositions*

The assemblage of major minerals in D'Orbigny (as in other angrites) is out of equilibrium (e.g., Prinz et al., 1977, 1990). The presence of Ca-rich olivine (La ~19 mol.%) and kirschsteinite (La ~33 mol.%) is incompatible with the presence of anorthite because they are stable only under very low Si activity (see Prinz and Weisberg, 1995). Consequently, melilite would be the proper co-existing Al-bearing phase, which we do not see.

The chemical compositions of co-existing phases are also far out of equilibrium as forsterites co-exist with titaniferous aluminous hedenbergite and kirschsteinite. The major phases such as olivine and augite are not compositionally zoned in a way one would expect for phases growing from a compositionally continuously changing melt. These phases are rather characterized by a large, compositionally homogeneous core that is overgrown by one or more very Fe-rich rims (see Figs. 10, 11 and Mikouchi et al., 1996, 2001). The compositional range must reflect events taking place under changing conditions, which apparently changed in only one direction: the events became increasingly more oxidizing from one to the other. The early events very likely were reducing, possibly with high S activity. The first oxidizing event was mild but efficient: it caused exchange of Mg for Fe in olivines. The relictic composition of this event is only preserved in the olivine megacrysts, in olivinites and in spinels. As this event managed to compositionally change sizeable crystals and to produce homogeneous grains it likely took place at elevated temperature. The Fe-Mg exchange apparently was accompanied by Mn-Mg and

Cr-Mg exchanges. As the newly established FeO/MnO ratio is close to that of CI chondrites (91 and 94, respectively, Anders and Grevesse, 1989), the source of these elements likely also had a chondritic FeO/MnO ratio.

In addition to Fe, Mn and Cr, the second oxidation and mobilization event affected practically all elements and created the main mass of augite grains. It appears to be recorded in the cores of the small olivines (of the anorthite-olivine intergrowths) and in the cores of the large augites. These phases have molecular Fe/Mg ratios between 0.55 (olivines) and 0.80 (augites). Olivines and augites seem not to be in chemical equilibrium with respect to the Fe/Mg ratio. As the FeO/MnO ratio of the olivine is again similar to that in CI chondrites (92 vs. 94, respectively), the source for these two elements likely also had a chondritic Fe/Mn ratio. The augite has a fractionated Fe/Mn ratio which is due to the preferential partitioning of Mn into clinopyroxene compared to olivine ( $D_{\text{Mn}}(\text{ol-cpx}) \sim 2$  compared to  $D_{\text{Fe}}(\text{ol-cpx}) \sim 3.5$ , e.g., Duke, 1976; Irving, 1978; Green, 1994).

The other major elements necessary to grow augite pneumatically, such as Ca, Ti, Al and Si, could have been mobilized from preexisting phases. As Ca, Al and Ti are highly refractory elements under solar nebula (i.e., reducing) conditions, they likely were present in condensed phases, possibly in those constituting the solid spheres (which at this point are already shelled). An oxidizing event could have mobilized these elements, all of which form volatile species under such conditions (e.g., Hashimoto, 1992). This mobilization and reprecipitation event changed the rock into what it is basically now: an anorthite-olivine-augite rock with empty shells and abundant druses. The latest event produced the practically Mg-free mineral assemblage Ca-rich olivine, kirschsteinite and titaniferous aluminous hedenbergite, all with atomic Fe/Mg ratios  $> 40$ . A silico-phosphate and a Fe-Ti-Al-silicate, two new and so far not described phases (see also Mikouchi and McKay, 2001; Mittlefehldt et al., 2001) very likely also belong to this assemblage. Co-existing Ca-rich olivine and kirschsteinite indicate a formation T of about 1000 °C (Davidson and Mukhopadhyay, 1984). As at such a temperature diffusion rates for Fe and Mg are fairly high in olivine (e.g., Buening and Buseck, 1973), this late Fe, Ca veneer probably lasted only for a relatively short time, otherwise the steep compositional gradients in olivine would have been erased. For firm data additional studies will be necessary.

Trace element abundances in major phases (Floss et al., 2001; Kurat et al., 2001c, 2003) are high and seem to be out of equilibrium with a possible parental melt of bulk D'Orbigny chemical composition. In particular, abundances of high field strength ions in augite are much too high, by factors of 10 and more (Kurat et al., 2001c). On the other hand, the Sc content of late titaniferous aluminous hedenbergite is only 0.1–0.3 times that of the druse augite, but equilibrium crystallization calculations predict a Sc content which is two times that of the druse augite. Clearly, augite and titaniferous aluminous hedenbergite cannot have crystallized from the same liquid. In particular, the source of titaniferous aluminous hedenbergite—liquid or vapor—was strongly depleted in Sc as compared to the source of the augite cores.

In summary, the minerals co-existing in D'Orbigny are out of equilibrium. They likely document successive events in

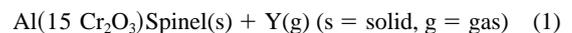
which vapor-solid exchange reactions and solid-vapor-solid mobilizations created the rock as it is now. The processes took place at successively lower temperature and at increasing oxygen fugacity. The latest event that created voluminous overgrowths on olivines and augites was highly oxidizing, took place at about 1000 °C and under strongly silica-undersaturated conditions and possibly lasted only for a short time.

### 5.3.4. Unstable spinel

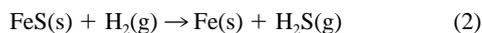
Aluminous spinel is a very early phase in D'Orbigny because it is included by early olivine and anorthite—as well as by augite. This is surprising because spinel should not be on the liquidus of a melt with the chemical composition of a basaltic angrite (e.g., Longhi, 1999). According to Kamenetsky et al. (2001), a spinel with 48 wt.%  $\text{Al}_2\text{O}_3$  can be in equilibrium with a melt which contains about 20 wt.%  $\text{Al}_2\text{O}_3$ —but D'Orbigny has only 13–14 wt.%  $\text{Al}_2\text{O}_3$ . Consequently, spinel in D'Orbigny has to be considered to be “xenocrystic”—another one in addition to olivine, which makes two important minerals that do not belong to the rock, if we believe this rock to be of igneous origin.

Longhi (1999) succeeded in getting spinel in angrites by “. . . following crystallization of ol + aug + plag, the plagioclase reacted completely at the plagioclase-peritectic with the interstitial liquid, which subsequently crystallized beyond the plagioclase peritectic onto the ol + aug + sp liquidus boundary curve.” However, this does not work in the case of D'Orbigny because, texturally, spinel is a very early phase that is enclosed by olivine-anorthite intergrowths. In addition, as can be seen in Figure 12A, some spinels record a complex history before they found shelter in olivine and anorthite. Furthermore, spinels should not carry Cr when formed late in the crystallization history of the rock, because this element would not be available at this stage anymore (see also Mittlefehldt et al., 2002).

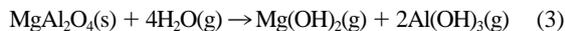
Not only is spinel not stable in a melt of angrite composition, it was also not stable before it was captured for D'Orbigny by olivine and anorthite. It is commonly covered by a reaction zone (Fig. 12A), which has previously been described as “symplectic” (e.g., Mittlefehldt et al., 2002). However, a look at Figure 12A 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. Consequently, what D'Orbigny spinels indicate is a reaction that took place *before* they were captured by anorthite and/or olivine. As we see only one reaction product now, namely Cr-bearing Al-spinel, the second must have been lost. The situation suggests that spinel sometime in its history, but before olivine and anorthite crystallized, became unstable and a spinel that is richer in Cr than the original one became stable according to:



The texture suggests decomposition of the  $\text{Al}(7.5 \text{ Cr}_2\text{O}_3)\text{Spinel}$  and massive mass loss—similar to, e.g., the decomposition of troilite into metal and  $\text{H}_2\text{S}$  or  $\text{S}_2$  (compare Figs. 2 and 3 of Tachibana and Tsuchiyama, 1998) according to the reaction:



We may speculate that the unknown reactant X in Eqn. 1 could have been H<sub>2</sub>O taking place in the partial reaction:



which leaves a residual spinel enriched in FeCr<sub>2</sub>O<sub>4</sub>, a possible reaction according to experimental results of Hashimoto (1992). The reaction obviously remained incomplete, leaving a highly porous envelope of spinel enriched in (Mg,Fe)Cr<sub>2</sub>O<sub>4</sub> over the original composition. It is also obvious that this porous envelope around Al-spinels never could have survived encounter with an angritic silicate melt. The pores of the reaction rims must have been filled with olivine and anorthite in a very gentle, non-disturbing way. This appears only to be possible via a fluid with no wetting problems.

Spinel carries also another important message: they apparently were present very early in the history of D'Orbigny and they possibly contained Cr and Fe *before* they were captured by olivine and anorthite. Consequently, oxygen fugacity was already high enough to support Fe<sup>2+</sup> in spinel before anorthite-olivine intergrowths formed. Spinel cores seem not to be in equilibrium with either olivine megacrysts or the cores of matrix olivines with respect to Fe and Mg with the atomic  $K_d = (\text{Mg/Fe})_{\text{olivine}}/(\text{Mg/Fe})_{\text{spinel}}$  being about 4 and 8 for these pairs, respectively (Table 2). This is far above the equilibrium value of about 2.5 (e.g., Kamenetsky et al., 2001). Manganese was apparently not available when the spinel composition was established. This poses a problem because all olivines do contain Mn<sup>2+</sup>, which even is in an approximate chondritic abundance proportion to Fe<sup>2+</sup>. As only the spinel of the reaction rim contains some Mn, we have to conclude that the composition of the spinel core was established in an event before the reaction rim and olivine and anorthite formed.

### 5.3.5. Glasses

The chemical composition of the most common glasses filling voids and hollow spheres (Table 2) resembles that of angrite bulk rocks but is at the lower end of the range for the angrite bulk MgO contents (except for LEW 86010) and the CaO/Al<sub>2</sub>O<sub>3</sub> ratio (except for LEW 87051) and at the higher end of the range for the FeO content (except for Asuka 881371 and Sahara 99555). Glasses have superchondritic Ca/Al ratios (Varela et al., 2001a, 2003a, 2003b) and their contents of FeO and TiO<sub>2</sub> are within the range of the angrites bulk rock composition (e.g., Varela et al., 2003a, 2003b).

The abundances of the refractory elements Ti, Al and Ca are about 10 × CI abundances and their ratios are close to their ratios in chondrites. Especially the CaO/TiO<sub>2</sub> ratio (17 compared to 18 in chondrites) appears to be unfractionated as does the FeO/MnO ratio (86 vs. 94). Thus, the glasses also register a source that had some elements in chondritic abundance proportions. It is indeed remarkable that not only the FeO/MnO ratio but also the FeO and MnO abundances in D'Orbigny glass are similar to those in CI chondrites (23.3 vs. 23.4 wt.% and 0.27 vs. 0.25 wt.%, respectively, see Varela et al., 2003b and Anders and Grevesse, 1989).

The D'Orbigny glasses are similar in composition to bulk Asuka 881371 as reported by Prinz and Weisberg (1995) and to

YA 1154 (Yanai, 2000) but not to those reported by Nazarov et al. (1995) for angritic rock fragments in the Erevan howardite. Apparently, melts of angrite composition existed, albeit in small amounts, and in some cases were chilled to fine-grained rocks. D'Orbigny for yet unknown reasons retained glasses instead of such chilled rocks.

Glasses can very well be considered remnant melts from which angrites could in principle have crystallized, as they can precipitate olivine, augite and plagioclase (CIPW-norm has An: Di: Ol ~1: 1: 1). However, glasses fill former empty space and, thus, clearly were added after the formation of open space, especially, after dissipation of one of the early sphere-forming phases. All shells apparently were not available at this stage as only some of them are filled by glass. Another possibility is that melt (the precursor of the glass) was present only in small amounts, mainly wetting the surfaces in interstitial space and facilitating growth of large crystals from the vapor, as has been suggested for the growth of C chondrite forsterites (e.g., Varela et al., 2002). This, in principle, is one possible way to form the glass which could represent such a quenched melt. This is also the conclusion reached by Varela et al. (2003b) in their study of D'Orbigny glasses.

Shock as a heat source for the formation of glasses has to be excluded as no shock features are present but very delicate structures like the hollow spheres are. Also, the Pb age of the glass is indistinguishable from that of D'Orbigny itself (Jotter et al., 2002, 2003).

The trace element contents of the most common glasses in D'Orbigny are very similar to those of bulk angrites, eucrites (e.g., Kitts and Lodders, 1998; Kurat et al., 2003b), Allende chondrule matrices (Kurat et al., 1992) and glass inclusions in olivines of C chondrites (Varela et al., 2002). A primary solar nebula origin thus seems not to be excluded (see Yoneda and Grossman, 1995; Ebel and Grossman, 1999), a possibility which is dealt with in a separate report (Varela et al., 2003b).

In summary, glasses have chemical compositions related to bulk angrite rocks, angritic melt rocks, eucrites, chondrule matrices and glass inclusions in C chondrite olivines. Apparently, some melt was present late in the history of the rock. In contrast to other angrites such as Asuka 881371, the melts in D'Orbigny were chilled to glass instead of a fine-grained rock. The source of the melts could have been the solar nebula vapor—similar to glasses of glass inclusions in C chondrite olivines (e.g., Varela et al., 2002, 2003b).

### 5.3.6. Bulk chemical composition

Bulk major and trace element abundances in D'Orbigny are similar to those in other angrites (Table 4, Fig. 13). The trace element abundances are also similar to those in D'Orbigny glasses (Varela et al., 2001a, 2003b) and also similar to those in eucrites (e.g., Kitts and Lodders, 1998), in glasses of glass inclusions in olivine of the Renazzo CR chondrite (Kurat et al., 1997; Varela et al., 2002) and in matrices of Allende chondrules (Kurat et al., 1992). The unfractionated abundances of the refractory lithophile elements (at about 10 × CI abundances, see Fig. 13a) indicate a derivation from a primitive chondritic source without involvement of geochemical processes like partial melting. The small deficit in Sc is unexplained but can be taken as to indicate removal of a Sc-bearing

phase from the system before angrite formation. This could be due to crystallization of olivine (mega-crystals), but as it is accompanied by a similar deficit in Al, we may speculate that a refractory Al-phase was involved. However, considering the many alteration events D'Orbigny has encountered (and the other angrites probably too), a minor loss of Sc can be envisaged also to have occurred during mobilization of Ca, Al and Ti, which possibly was accompanied by mobilization of Sc too. Because the Ca/Ti ratio and other ratios of refractory elements still are chondritic, only Al and Sc appear to have been lost. The strong depletion of D'Orbigny (and other angrites) in the volatile lithophile elements indicates a vapor fractionation—similar to what is seen in glasses of glass inclusions (Kurat et al., 1997; Varela et al., 2002) and what is commonly observed in CAIs and chondrules from C chondrites (e.g., Martin and Mason, 1974; Grossman, 1980; Kurat et al., 1985). The depletion in siderophile elements as compared to the refractory lithophile elements is also reminiscent of similar depletions present in chondrules from C chondrites (e.g., Kurat, 1985; Rubin and Wasson, 1987). The normalized abundances of Ni, Co and Fe are 0.0026, 0.066 and  $0.975 \times \text{CI}$ , respectively, which correspond to the apparent CI/D'Orbigny distribution coefficients of 385, 15 and 1, respectively. The ratio  $15/385 \sim 0.04$  corresponds approximately to the ratio of the respective liquid distribution coefficients  $D_{(\text{metal/silicate})}$ ,  $D^{\text{Co}}/D^{\text{Ni}} = 89/1700 \sim 0.05$  for  $\log f\text{O}_2 = -12.4$ ,  $T = 1250\text{--}1275$  °C (Newsom, 1990), indicating a metal-silicate fractionation event. This event involved metal with a primitive chondritic Ni/Co ratio and should have taken place at slightly more oxidizing conditions than those represented by the distribution coefficients used above.

Iron has a strong positive abundance anomaly in D'Orbigny, which is obviously due to its late addition in the oxidized state (together with Mn), similar to what is exhibited by many chondrules from carbonaceous and other chondrites (e.g., Kurat et al., 1985). The chondritic abundances of Fe (Fig. 13B) and Mn (Fig. 13A) cannot be a coincidence but rather indicate co-mobilization of these elements from a chondritic source and co-precipitation in the D'Orbigny angrite.

In summary, the trace element abundances indicate formation of D'Orbigny as a refractory condensate from a source with chondritic abundances of refractory lithophile elements, except Al and Sc. Fractionation of lithophile from siderophile elements took place between a primitive metal and silicate. Subsequently, the rock experienced metasomatic alterations which were fed from a chondritic source and led to enrichments (relative to the original composition) in the moderately volatile species FeO and MnO, among others.

### 5.3.7. Summary D'Orbigny

D'Orbigny can be petrographically described as a miarolitic dolerite containing hollow shells. It is an angrite with all properties—bulk chemical composition, mineralogical composition, mineral chemistry, rare gas contents and O isotope abundances—in line with the other five members of this meteorite class. Its cosmic ray exposure age is unique and excludes pairing with any other angrite known.

The shape of D'Orbigny, its structure with highly porous lithologies alternating with compact ones and its mineralogical

heterogeneity strongly suggest that the rock was not formed by simple crystallization of a basaltic melt. The mushroom-like aspect of D'Orbigny and the alternating texturally different layers are suggestive of a directional growth structure. Growth apparently began on top of a round object (the back side pan-like shield must be a negative replica of a preexisting object) with the formation of a fine-grained, low-porosity lithology which later became the back shield of the meteorite. On top of that lithology radially fingering aggregates and plates of anorthite-olivine intergrowths formed a highly porous rock with very abundant large elongated voids which now house mainly euhedral augite and some anorthite crystals. Changing conditions caused continuing growth forming again a fine-grained, low-porosity lithology which later became the front shield of the meteorite.

D'Orbigny is a heterogeneous mixture of a few constituents or building blocks. The hollow shells, olivine megacrysts and olivinite objects appear to be the oldest building units. The now hollow shells are very likely morphologic copies of solid spheres (of an unknown compound, maybe CaS), possibly the earliest phase present during formation of the rock. These spheres were covered by anorthite-olivine intergrowths at the earliest stage of rock formation. Together with the solid spheres also freely growing anorthite-olivine intergrowths and plates aggregated, forming a fluffy fractal skeleton. Depending on local growth conditions, the aggregate (proto-rock) consisted of fine-grained or coarse-grained constituents. This took place under mildly oxidizing conditions and led to the mineral association: an unknown phase (CaS? spheres), anorthite-forsterite intergrowths, forsterite megacrysts and olivinites and minor Cr-bearing Al-spinel. With changing redox conditions, the reduced phase(s) constituting the solid spheres became unstable, disintegrated and were transformed into mobile chemical species one of which likely was  $\text{Ca}(\text{OH})_2$ . During this event large quantities of oxidized Fe (plus Mn, Cr) became available in the vapor phase which was likely fed by a source which had a chondritic Fe/Mn ratio. Olivine began to exchange Mg for Fe, Mn and Cr and augites started to grow either by replacing some of the olivine or filling the plentiful voids. Some of the voids managed to become closed, others remained open. The solid cores of the spheres were subsequently lost, leaving the anorthite-olivine shells empty. Only minor residual carbonate with non-terrestrial Sr and Pb isotopes was occasionally left behind (Jotter et al., 2002). A late, highly oxidizing event created the titaniferous aluminous hedenbergite, Ca-rich olivine and kirschsteinite rims on augites and olivines, respectively. Oxidation conditions must have been severe to provide mobility for Ca and Ti, probably took place at about 1000 °C and lasted only for a short time. The decomposing sphere phase(s) could have supplied the Ca for the augites and may also have supplied the Ca necessary for the formation of kirschsteinite. Remarkably, the very large voids of the druses were not filled by the precipitates of this late event.

Among the early events must have been the precipitation of glasses into interstitial space. Glasses have chemical compositions related to bulk angrite rocks and rare angritic melt rocks and were formed early in the history of D'Orbigny possibly from melts. For unknown reasons the melt was chilled to glass instead of crystallizing into a fine-grained rock (as in LEW 87051, Mikouchi et al., 2000b, or the angritic fragment YA

1154 of Yanai, 2000). The melt could be a remnant of a silicate liquid that facilitated growth of the olivine megacrysts, large anorthites and anorthite-olivine intergrowths from the vapor (see Varela et al., 2003b for more details). As all other phases, the glass was also subject to vapor-solid exchange reactions and likely attained its Fe/Mg and Fe/Mn ratios and its high contents of medium volatile elements by this process.

The trace element abundances in D'Orbigny do not indicate any geochemical (i.e., crystal-liquid) fractionations, which are expected for igneous rocks that usually form from liquids created by partial melting of a source more refractory than the partial melts. Instead, the trace element abundances indicate formation of D'Orbigny as a refractory precipitate from a source with chondritic abundances of refractory lithophile elements. Abundances of Ni and Co indicate siderophile—lithophile element fractionation in the presence of a chondritic metal. As the subsequent metasomatic alterations also appear to have been fed from a chondritic source, the whole formation environment of D'Orbigny appears to have been a chondritic one.

## 6. SKETCHING A NEW MODEL FOR ANGRITE FORMATION

Prinz et al. (1988, 1990), Prinz and Weisberg (1995) and Longhi (1999) concluded that angrites definitely must have some relationship to CAIs. They tried to fit this perception into the igneous model of angrite genesis (see above). Prinz and Weisberg (1995) speculated on the possibility of CAIs being the source of angritic liquids whereas Longhi (1999) suggested that a CAI component was mixed into a melt derived as a partial melt from an unknown but somehow chondritic precursor. However, while no chondritic rock without alkalis exists, plenty of CAIs are known to carry this feature. The straightforward conclusion that angrites are a special form of CAIs apparently was not possible because of the high FeO and MnO contents of angrites being in stark contrast to the low ones of CAIs. In terrestrial petrology, the Fe/Mg ratio is an important and reliable indicator of the degree of fractionation of a rock. This is because terrestrial melts evolve from the upper mantle, a vast and fairly well equilibrated reservoir. The situation for meteorites differs from that principally as their Fe/Mg ratios are likely to be of secondary origin (e.g., Kurat, 1988) in spite of the vast common reservoir, the solar nebula. As the Fe/Mg ratio of solids or liquids formed in the solar nebula will depend on the redox conditions prevailing during their formation, we can expect an extreme diversity of this ratio among meteorites, which we do indeed observe. For the case of angrite genesis this means that the Fe/Mg ratio of the rock records a strong late metasomatic Fe-Mg rock-vapor exchange event and that it is not related to the primary formation of the rock. Taking this fact into account, we arrive at a simple scenario for angrite genesis: they are CAIs that grew larger than the ones we know from C chondrites and they have seen and recorded a variety of changing environmental conditions. Apparently, conditions changed from highly reducing ones early in their history to late strongly oxidizing ones, a situation also commonly observed for CAIs (e.g., Kurat et al., 2002). Thus, it is likely that angrites record rare and special conditions in some part of the early solar system and detailed studies of these peculiar rocks can provide us with a detailed picture of this peculiar place.

It is certainly no coincidence that individual angrites and CAIs can have their individual histories—as chondrules have their individual histories. Because CAIs can be solid solar nebula condensates (e.g., Grossman, 1972, 1980) as well as evaporative residues (Kurat, 1970) and they can have igneous as well as granoblastic textures and aggregation structures, we may expect to find angritic counterparts to all these different types. Indeed, angrites reproduce most of the textures and structures of CAIs: there are crystallized liquids (Asuka 881371, LEW 87051), metasomatic granoblastic rocks (LEW 86010, Angra dos Reis?) and at least one aggregate (D'Orbigny). Only evaporative residues are missing. In addition, most CAIs record metasomatic alterations, subsolidus processing after their formation, also exactly what is recorded by all angrites.

The formation of large objects like D'Orbigny, large volumes of silicate liquids (glass in D'Orbigny, liquids for LEW 87051 and Asuka 881371), formation of megacrysts and the early appearance of Fe<sup>2+</sup> indicate high partial pressures of the condensable elements early in the history, possibly due to a high dust/gas ratio (e.g., Yoneda and Grossman, 1995; Ebel and Grossman, 1999). This is also in line with the extremely oxidizing conditions recorded by angrites late in their history, which should need very high dust/gas ratios—a subject not yet investigated.

Considering the chemical similarities between angrites, eucrites (Kitts and Lodders, 1998), CAIs (Grossman, 1980), Allende chondrule mesostasis (Kurat et al., 1992), basaltic objects in C chondrites (Kurat and Kracher, 1980) and glass inclusions in olivines of C chondrites (Kurat et al., 1997; Varela et al., 2002), refractory matter appears to have been wide-spread in the solar nebula. It was present as solids and commonly also as silicate liquids. Most of the liquids crystallized subsequently but some were chilled to glass. The roots of all these materials seem to be refractory solar nebula condensates—liquid ones as well as solid ones (e.g., Grossman, 1972; Yoneda and Grossman, 1995; Kurat et al., 2003b). The diversity displayed now is likely due to differences in formation conditions and post-formation processing (e.g., Kurat, 1988; Kurat et al., 2002).

Angrites differ from CAIs principally in their very low refractory siderophile element contents, a feature they share with eucrites and with some glass inclusions in olivine of C chondrites. An early separation of refractory siderophile from the refractory lithophile elements is indicated and supported by Hf-W isotope data (e.g., Quitté et al., 2000). The siderophile element contents of angrites (and eucrites), however, are not on a constant low level but rather highly variable indicating variable efficiency of the separation process. Some similarity with the siderophile element depletions in chondrules is apparent. At present we do not understand this part of angrite genesis yet but we are going to investigate it.

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