



## The non-igneous genesis of angrites: Support from trace element distribution between phases in D'Orbigny

María Eugenia VARELA,<sup>1\*</sup> Gero KURAT,<sup>2</sup> Ernst ZINNER,<sup>3</sup> Peter HOPPE,<sup>4</sup>  
Theodoros NTAFLIOS,<sup>2</sup> and Mikhail A. NAZAROV<sup>5</sup>

<sup>1</sup>CONICET-UNS, Dpto. Geología, San Juan 670, (8000) B. Blanca, Argentina

<sup>2</sup>Institut für Geologische Wissenschaften, Universität Wien, Althanstrasse 14, A-1090 Vienna, Austria

<sup>3</sup>Laboratory for Space Sciences and Physics Department, Washington University, Saint Louis, Missouri 63130, USA

<sup>4</sup>Abteilung Kosmochemie, Max-Planck-Institut für Chemie, Postfach 3060, D-55020 Mainz, Germany

<sup>5</sup>Vernadsky Institute, RAS, 119991 Moscow, Russia

\*Corresponding author. E-mail: [evarela@criba.edu.ar](mailto:evarela@criba.edu.ar)

(Received 18 August 2004; revision accepted 20 December 2004)

**Abstract**—D'Orbigny is an exceptional angrite. Chemically, it resembles other angrites such as Asuka-881371, Sahara 99555, Lewis Cliff (LEW) 87051, and LEW 86010, but its structure and texture are peculiar. It has a compact and porous lithology, abundant glasses, augite-bearing druses, and chemical and mineralogical properties that are highly unusual for igneous rocks. Our previous studies led us to a new view on angrites: they can possibly be considered as CAIs that grew to larger sizes 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. Here we report trace element contents of D'Orbigny phases. Trace element data were obtained from both the porous and the compact part of this meteorite. We have confronted our results with the popular igneous genetic model. According to this model, if all phases of D'Orbigny crystallized from the same system, as an igneous origin implies, a record of this genesis should be expressed in the distribution of trace elements among early and late phases. Our results show that the trace element distribution of the two contemporaneous phases olivine and plagioclase, which form the backbone of the rock, seem to require liquids of different composition. Abundances of highly incompatible elements in all olivines, including the megacrysts, indicate disequilibrium with the bulk rock and suggest liquids very rich in these elements ( $>10,000 \times$  CI), which is much richer than any fractional crystallization could possibly produce. In addition, trace element contents of late phases are incompatible with formation from the bulk system's residual melt. These results add additional severe constraints to the many conflicts that existed previously between an igneous model for the origin of angrites and the mineralogical and chemical observations. This new trace element content data, reported here, corroborate our previous results based on the shape, structure, mineralogy, chemical, and isotopic data of the whole meteorite, as well as on a petrographic and chemical composition study of all types of glasses and give strength to a new genetic model that postulates that D'Orbigny (and possibly all angrites) could have formed in the solar nebula under changing redox conditions, more akin to chondritic constituents (e.g., CAIs) than to planetary differentiated rock.

### INTRODUCTION

Angrites are a small group of augite-anorthite-olivine rocks with apparent formation ages similar to those of chondrites: the U-Pb, Th-Pb, and Pb-Pb ages for Angra dos Reis, LEW 86010, and D'Orbigny are between 4.54 and 4.5578 Ga (Wasserburg et al. 1977; Lugmair and Galer 1992; Jagoutz et al. 2002). The genesis of these rocks is highly

controversial, as shown by their mineralogical composition, petrology, geochemistry, and isotopic features (Prinz et al. 1977, 1988; Goodrich 1988; McKay et al. 1988, 1990; Prinz and Weisberg 1995; Mikouchi et al. 1996; Mikouchi and McKay 2001). Recent petrographic and geochemical studies of the dense part of D'Orbigny suggest that this rock formed from a melt by rapid and complete crystallization (Mittlefehldt et al. 2001, 2002). However, the mineralogical,

mineral, and bulk chemical properties of angrites remain peculiar because all phases are usually out of equilibrium (Prinz and Weisberg 1995; Kurat et al. 2001a, 2001b, 2004). Specifically, the high abundances of refractory lithophile elements combined with high abundances of the moderately volatile elements Mn and Fe<sup>2+</sup> and low abundances of siderophile and volatile elements (e.g., Mittlefehldt et al. 1998) pose severe petrogenetic problems. In addition, the abundances of refractory elements are unfractionated with respect to solar abundances at the 10 × to 15 × CI level, very similar to what is observed in eucrites and Ca- and Al-rich inclusions from carbonaceous chondrites (Prinz et al. 1988, 1990; Prinz and Weisberg 1995). There are many problems with the distribution of certain trace elements between the phases in D'Orbigny. Such discrepancies for D'Orbigny and other angrites have been reported by Floss et al. (2003), who suggested that kinetic effects during fast crystallization could be the cause. Clearly, as has been previously recognized by Prinz et al. (1988, 1990), Prinz and Weisberg (1995), and Longhi (1999), there is no simple way to create this class of rocks.

The shape, structure, and texture of D'Orbigny and its mineral and bulk chemical compositions indicate a complex genesis under changing redox conditions, as do many constituents of chondrites (e.g., Kurat 1988; Kurat et al. 2002; Varela et al. 2002). Our observations on the textural features and data of major chemical compositions of all phases (Kurat et al. 2004), as well as the petrographic and chemical composition of all types of glasses present in D'Orbigny (Varela et al. 2003), are incompatible with a planetary igneous origin for this rock and support an origin related to that of Ca- and Al-rich inclusions in carbonaceous chondrites. Here we report trace element abundances of the different phases in the compact and porous part of D'Orbigny. The results support our previous conclusions and strengthen the view that angrites are rocks that record special conditions in the early solar nebula. Short preliminary reports were given by Kurat et al. (2001a, 2001b, 2003).

## ANALYTICAL TECHNIQUES

Mineral phases were analyzed for their trace element contents with the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) facility at Memorial University of Newfoundland. The instrument is a VG PlasmaQuad 2S+ ICP-MS coupled to a 266 nm NdYAG laser built in-house. The ICP-MS instrument is equipped with a fast-switching quadrupole mass filter and a single Galileo-type electron multiplier. The laser beam is focused through the objective of a microscope onto the sample surface. A 50 cm<sup>3</sup> sample cell is mounted on the computer-driven motorized stage of the microscope. The laser was set up to produce an energy of 1.5 mJ/pulse (measured just before the beam entered the objective of the microscope) at a repetition rate of 10 Hz with the laser beam focused about 200 μm above the surface

in order to produce a spot of about 50 μm on the sample surface. The cell was flushed with He gas during ablation to minimize fallback of ejecta and thus maximize analytical sensitivity. Typical data acquisitions consisted of a 60 sec measurement of the gas blank before the start of ablation, which lasted another 60 sec. Laser ablation produced a pit in the sample about 50 μm wide and 60 μm deep. Raw ICP-MS data were corrected for electron multiplier dead time (20 ns) and processed offline using a spreadsheet program (LAMTRACE, S. Jackson, unpublished) to integrate signals, subtract the gas blank, and calculate concentrations. Measurements on meteoritic samples were calibrated against the NIST SRM 612 standard using the concentration values of Pearce et al. (1997). Silicon, determined by EMP analysis, was used as the internal standard.

To avoid contamination by surrounding phases, the trace element contents of small phases were measured with the Cameca IMS 3F ion microprobes at Washington University, St. Louis, and the Max-Planck-Institut für Chemie in Mainz, following a modified procedure of Zinner and Crozaz (1986).

## RESULTS

The investigated samples were the polished sections D'Orbigny C, D'Orbigny D, D'Orbigny G, D'Orbigny XA, and mineral separates from rock specimens and rock debris D'Orbigny B2 (all from the Naturhistorisches Museum in Vienna).

The phases analyzed for trace elements were selected following the detailed petrographic and chemical study undertaken by Kurat et al. (2004), a brief summary of which is given below. This overview will help the reader understand the structure and textures of this rock, its minerals (e.g., olivines, augites, and anorthite), and their occurrence (e.g., in druses, shells, or plates). It will also provide information on the location of the phases that were analyzed.

### The Rock and Its Constituents

The D'Orbigny meteorite has a peculiar shape, resembling a loaf of bread. Its front and back shields are made of a compact lithology and the space between these shields is filled by a highly porous lithology, very rich in open druses and hollow shells.

Hollow shells, mostly perfectly spherical vugs with diameters from <1 mm to ~2 cm, are present throughout the meteorite, but appear to be more abundant in the porous part than in the compact shields.

The following six sections describe the constituents of D'Orbigny.

#### *Compact Shield Rock*

This part has a medium-grained micro-gabbroic texture with little pore space and scattered, small, open or closed druses and spherical hollow shells. Occasionally, some very

thin (<1 mm) plates (up to ~10 cm long) consisting of plagioclase-olivine intergrowths are present. The transition to the porous lithology is gradual with increasing grain size, pore size, and abundances of druses and hollow shells. The compact micro-gabbro-like rock consists mainly of anorthite, olivine, and augite. The centers of olivines commonly display euhedral rhombic shapes with Ca-rich olivine-kirschsteinite intergrowths filling the intergranular space. Trace element analyses of phases belonging to the micro-gabbroic texture (either in the compact or porous part of the rock) will be referred to as anorthite micro-gabbro (mg), olivine mg, augite mg, spinel mg, and kirschsteinite. The late phases such as kirschsteinite, sulfides, ulvöspinel, Fe-Ti-Al silicate, silicon-phosphate, etc., only occur in the micro-gabbroic-texture part.

#### *Olivine Megacrysts and Olivinites*

These are more common in the porous part of D'Orbigny than in the rest. The olivine megacrysts are large green crystals; they are clear and transparent and are intimately intergrown with the host rock. Large olivinites (polycrystalline olivine) consist of large, clear, green olivine grains of up to 8 mm in diameter or of very fine-grained olivines forming milky, greenish-white olivinites (Fig. 1). These olivinites are also intimately intergrown with the host rock and are mostly accompanied by anorthite-olivine intergrowths. Trace element analyses on these phases are referred to as olivine mega and olivinite, respectively.

#### *Shells*

Hollow spherical shells are unevenly distributed throughout D'Orbigny; they are present in all parts, but are most common in the porous inner portion. The shell itself is a compact granular intergrowth of fine-grained anorthite and olivine (similar to the large plates, see below) and occasionally has some augite at the outside. In some places, olivine is more abundant than anorthite and has a tendency to be oriented perpendicular to the surface (Fig. 2). Trace element analyses on these phases are referred to as olivine shell and anorthite shell.

#### *Anorthite-Olivine Plates*

The compact and fluffy parts of D'Orbigny contain thin (~1 mm) but occasionally large (up to 10 cm long) plates consisting of anorthite-olivine intergrowths like the ones forming the shells (Fig. 3). The center of the plate consists of large anorthite grains that are intimately intergrown with mostly anhedral olivines (up to 100  $\mu\text{m}$ ), commonly in a graphic way, and rare euhedral Cr-bearing Al spinel (Fig. 3b). Trace element analyses on these phases are referred to as: olivine plate and anorthite plate. Two plate olivines are located in big plagioclase grains close to nests of ulvöspinel + sulfides in nearby vugs. The trace element compositions of these phases, as explained below, suggest that the Ca-rich olivines inside plagioclase are the products of late-stage metasomatism. These phases are referred to as Ca-rich Ol.

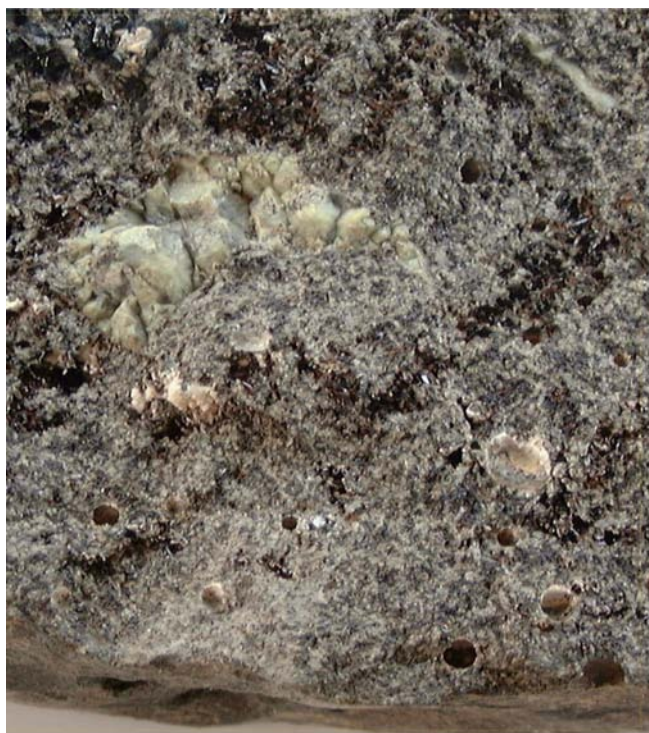


Fig. 1. Large olivinite (green), abundant druses with augites (brown), and hollow shells in the porous part of D'Orbigny. Some of the open spaces are partly filled by caliche (white). The fusion crust is visible at the bottom of the image. Width of the picture is 4 cm.

#### *Druses*

They are omnipresent in the porous portion of D'Orbigny. They are irregular, open spaces up to 3 cm or greater in elongation into which perfectly crystallized augites of prismatic habit and occasional anorthite plates protrude (Fig. 4). Trace element analyses on these phases are referred to as: augite druse. Ion microprobe analyses undertaken in the core are referred to as augite core. Aluminous hedenbergite is filling most of the intergranular space (Fig. 4b) and is present only when augite is in contact with other phases. In closed druses, it can be observed overgrowing augite crystals, forming a rim-like texture (see Fig. 10; Kurat et al. 2004). However, it is totally absent on augite crystals, protruding into open druses (Fig. 4b).

#### *Minor Phases*

Cr-bearing Al spinels are common and typically associated with olivine and plagioclase (small euhedral octahedra) in the olivine-plagioclase intergrowths, occasionally also with augite. They occur also as large, anhedral grains in the rock, mostly associated with olivine and plagioclase. Ulvöspinel is also common and occur typically as distorted skeletal crystals (hopper crystals) that are associated with late aluminous hedenbergite, kirschsteinite, sulfides, and occasionally silico-phosphate. An unknown Fe-Al-Ti-silicate was found in multi-phase pockets in anorthite. This phase forms euhedral crystals of up to

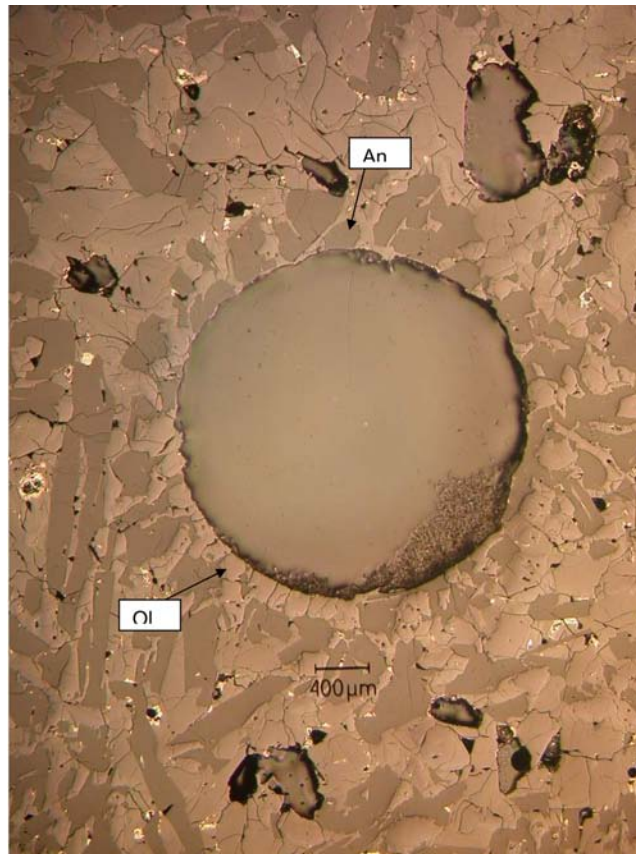


Fig. 2. Detail of a hollow shell consisting of anorthite-olivine intergrowths. Note the replicate of a former surface by the void surface and growth perpendicular to that surface. Reflected light picture.

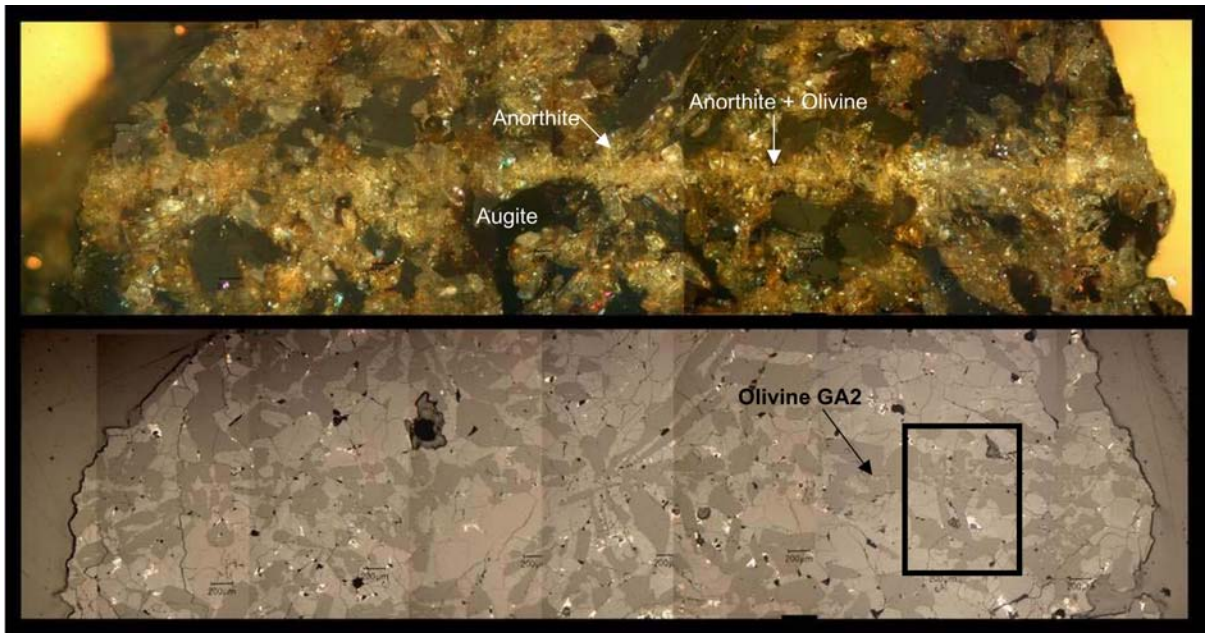
20  $\mu\text{m}$  diameter, is enclosed by augite, and associated with magnetite, troilite, and kirschsteinite. Trace element analyses on these phases are referred to as ulvöspinel and Fe-Al silicate.

### Trace Element Contents of Minerals

Olivines have highly variable trace element contents (Tables 1, 2, and 3). Rare earth element (REE) abundances range from Yb  $\sim 0.1 \times \text{CI}$  (abundance in CI chondrites) in olivine megacrysts (Fig. 5) to Yb  $\sim 1 \times \text{CI}$  in olivines from the micro-gabbroic rock and shells (Fig. 6) to Yb  $\sim 20 \times \text{CI}$  in kirschsteinites (Fig. 7). The abundance patterns are all fractionated with LaN  $\ll$  YbN (LaN and YbN: normalized to CI chondrite abundance). Olivine megacrysts and olivinites have the lowest TE contents with La and Yb abundances ranging from  $<0.001$  to  $\sim 0.2 \times \text{CI}$  and  $\sim 0.05$  to  $\sim 0.2 \times \text{CI}$ , respectively (Fig. 5). Olivine megacrysts are clearly poorer in all TEs than olivinites, except for Li, and are particularly poor in highly incompatible elements and in Cr and Mn. Trace element contents of olivines from shells and from the micro-gabbroic rock have La and Yb abundances of  $\sim 0.03$ – $0.3$  and  $0.7$ – $1 \times \text{CI}$ , respectively (Fig. 6). A similar range is also covered by olivines from a plate. A particular situation is

observed in some Ca-rich olivines located inside big plagioclase crystals (Ol. Ca-rich M and Ol. Ca-rich GA1). These olivines form part of a plate, but their chemical composition is different from that of the common olivines of the plate. They are extremely enriched in refractory trace elements (e.g., La  $\sim 2$ , Yb  $\sim 13 \times \text{CI}$ , Fig. 7). Abundances of other trace elements also vary over wide ranges, e.g., Zr from  $\sim 0.002 \times \text{CI}$  in olivinites to  $\sim 4.4 \times \text{CI}$  in Ol. Ca-rich GA1, Cr from  $\sim 0.001 \times \text{CI}$  in kirschsteinite to  $\sim 20 \times \text{CI}$  in Cr-bearing Al spinel (mg and plate), and Li from  $\sim 0.15 \times \text{CI}$  in olivinites to  $\sim 5 \times \text{CI}$  in plagioclase of the micro-gabbroic rock (mg) and shell (Fig. 8).

Trace element contents of augites vary within very narrow boundaries, except for the aluminous hedenbergite rims (Ferro-augite HH13, Fig. 9). Druse augite cores and augites from the micro-gabbroic rock (Aug. mg) have the same TE contents (Table 1, Fig. 9). They are rich in TEs and have an almost flat REE abundance pattern at  $\sim 10 \times \text{CI}$  with only small negative deviations for LREEs and Eu (Figs. 9 and 10). Normalized abundances of Zr, Ti, Sc, and V are at the same or at slightly higher level, but abundances of Nb, Sr, and the moderately volatile and volatile elements are much lower than those of the REEs. Aluminous hedenbergite rims have abundance patterns that approximately follow those of the



### Plate center

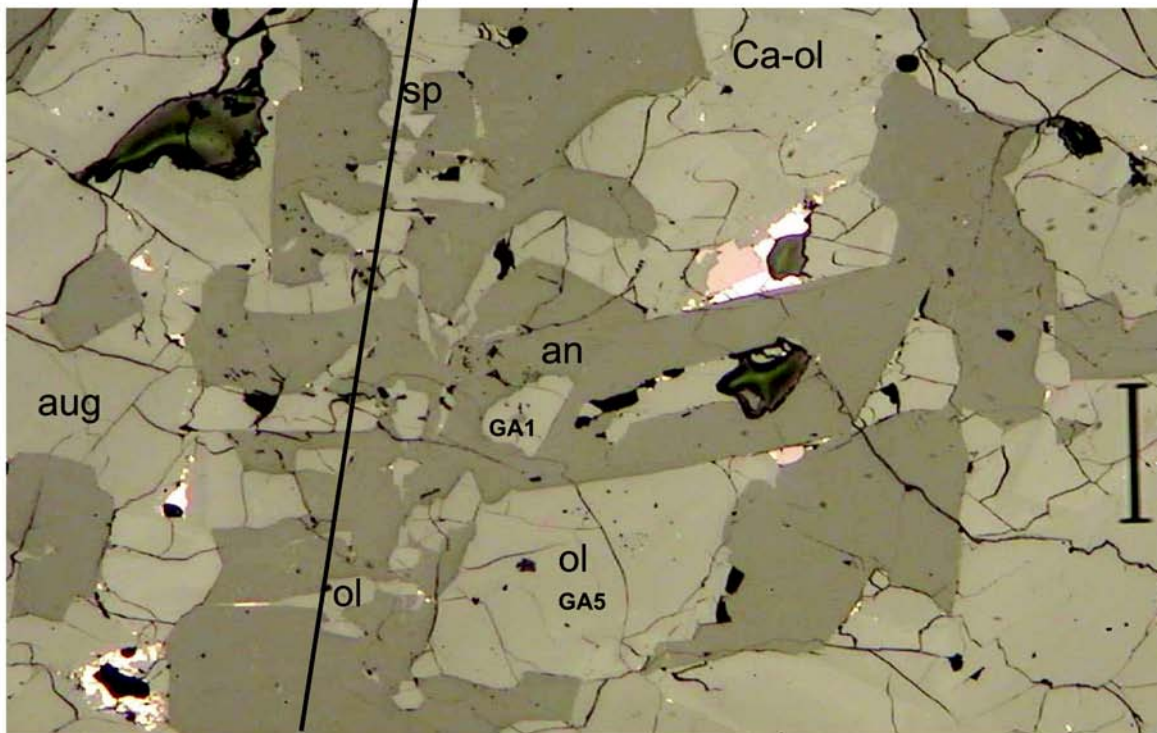


Fig. 3. a) Plate of anorthite-olivine intergrowth. The anorthite and the anorthite + olivine intergrowths form the clear brilliant plate with dark areas corresponding to augite. Both images are in reflected light, but the upper image was taken with crossed polarizers. Also indicated is the place of the olivine GA2. The square inset corresponds to Fig. 3b. Width of the sample is 11 mm. b) Detail of the anorthite + olivine plate. Olivine and Cr-bearing Al spinel (light gray), augite (gray), anorthite (dark gray). Also indicated are the olivines: GA1 (center), GA5 (center down), and Ca-Ol (upper right). Vertical scale bar: 200  $\mu\text{m}$ .

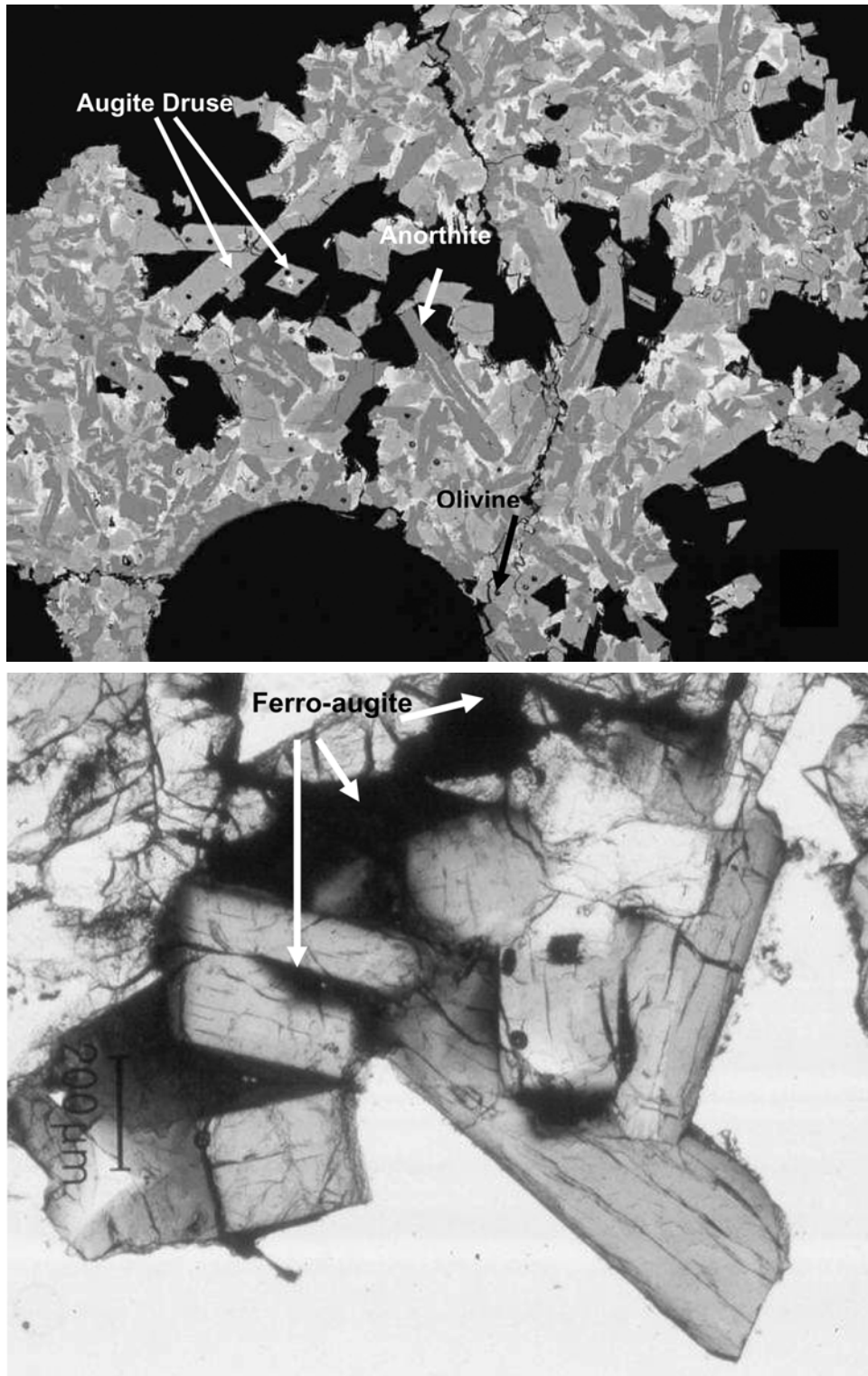


Fig. 4. a) Polished section of a hollow shell (bottom) and a druse with euhedral augites and anorthites protruding into the open space. Dots are ablation holes from LA-ICP-MS analyses. Backscattered electron (BSE) picture. Width of the picture is 10 mm. b) Augites in a open druse in D'Orbigny. Note the filling of the wedges by aluminous hedenbergite (black). Transmitted light picture.

Table 1. LA-ICP-MS analyses (in ppm) of olivines, augites and plagioclase from D'Orbigny.

Element	Olivine mega (2)	Olivinite (14)	Olivine mg (4)	Olivine shell (4)	Plag. shell (4)	Plag. mg (7)	Augite druse (10)	Augite mg (22)	Ferro-augite (1)
Li	0.39	0.42	2.10	1.76	6.13	5.78	1.02	1.12	1.23
Ca	2190	8090	7480	2190	153580	152920	162080	161980	160570
Sc	4.86	6.42	17	17	8.89	6.61	154	152	33
Ti	21	51	164.5	147.1	189	155	10000	9920	16450
V	12	16	31	34	10	6.30	562	616	58
Cr	192	1556	199	229	94	67	945	1085	
Mn	466	710	2912	2408	180	68	1280	1280	1320
Sr			1.24	3.43	228	240	19	18	37
Y	0.06	0.21	0.44	0.39	0.21	0.13	17	15	34
Zr		0.25	0.42	0.33	0.24		79	70	200
Nb		0.05	0.06	0.02	0.05	0.02	0.40	0.32	1.05
La		0.03	0.04	0.02	0.20	0.15	1.00	0.93	2.87
Ce		0.04	0.18	0.07	0.39	0.33	3.80	3.86	8.30
Nd		0.04	0.06	0.03	0.25	0.18	4.48	4.22	11
Sm		0.01	0.02	0.02	0.06	0.02	1.83	1.70	3.90
Eu			0.01	0.01	0.58	0.59	0.52	0.50	1.00
Tb							0.43	0.40	0.90
Gd		0.01	0.04	0.02	0.05	0.04	2.50	2.33	5.16
Dy		0.02	0.05	0.05	0.04	0.02	3.00	2.72	6.28
Ho			0.01	0.01			0.63	0.57	1.29
Tm			0.01	0.01			0.26	0.23	0.55
Yb	0.02	0.04	0.12	0.12	0.01	0.02	1.90	1.70	4.54
Lu			0.02	0.02			0.05	0.04	0.11

References: Plag. = plagioclase; mg = micro-gabbroic; (4) = number of minerals analyzed.

augite cores, but at levels between  $\sim 30$  and  $90 \times \text{CI}$ . A few elements do not follow the general pattern: Sc is much less abundant in the rims ( $\sim 5 \times \text{CI}$ ) than in the cores ( $\sim 30 \times \text{CI}$ ), as are V ( $\sim 0.1\text{--}1 \times \text{CI}$  versus  $\sim 10 \times \text{CI}$ ) and Cr ( $\sim 0.001\text{--}0.03 \times \text{CI}$  versus  $0.08\text{--}1 \times \text{CI}$ ) (Figs. 9 and 10).

Anorthite is generally poor in trace elements with REEs  $\sim 0.1 \times \text{CI}$ , except for Eu ( $\sim 8 \times \text{CI}$ ), and has a slight La/N > Yb/N fractionation (Fig. 11). Abundances of other trace elements are very low ( $< 0.1 \times \text{CI}$ ), except for Sr ( $\sim 30 \times \text{CI}$ ), Li ( $5 \times \text{CI}$ ), and Ti ( $\sim 0.3 \times \text{CI}$ ).

Cr-bearing Al spinel is also poor in trace elements with a flat REE pattern at  $\sim 0.1 \times \text{CI}$  (also Zr), but with high contents of Sc ( $\sim 1 \times \text{CI}$ ), V, and Cr ( $\sim 40 \times \text{CI}$ ) (Fig. 12). We analyzed a small spinel from a plate and a large one in the micro-gabbroic rock. Both showed the same trace element contents, but the analysis of the small grain showed some contribution from the surrounding anorthite, so we took the analysis of the big grain (see Fig. 12a of Kurat et al. 2004) to represent the spinel composition.

Ulvöspinel has fractionated REEs with La  $\sim 0.1 \times \text{CI}$  and Yb  $\sim 8 \times \text{CI}$ , high contents of Zr ( $\sim 100 \times \text{CI}$ ) and V ( $\sim 8 \times \text{CI}$ ), and very low Cr content ( $\sim 0.0004 \times \text{CI}$ ). The unnamed Fe-Ti-Ca-Al silicate (Mikouchi and McKay 2001; Kurat et al. 2004) is very rich in trace elements, with the REEs and Zr forming a flat pattern at  $\sim 100 \times \text{CI}$  and with Sr being slightly depleted ( $\sim 40 \times \text{CI}$ ), Sc depleted ( $\sim 2 \times \text{CI}$ ), and V and Cr strongly depleted ( $\sim 0.09$  and  $0.0002 \times \text{CI}$ , respectively) with respect to the refractory trace elements (Fig. 12).

## DISCUSSION

D'Orbigny is an angrite with chemical, isotopic, textural, and mineralogical properties resembling those of angrites previously described, such as Asuka-881371 and Sahara 99555 (Yanai 1994; Prinz and Weisberg 1995; Warren and Davis 1995; Bischoff et al. 2000; Mittlefehldt et al. 2002). Compositionally, D'Orbigny is almost identical to Sahara 99555 (Mittlefehldt et al. 2002), showing very similar REE abundances and distributions between phases (Floss et al. 2003). However, as mentioned before, the structure, some textural features, and the presence of augite druses and glass make D'Orbigny unique in this group. The shape of D'Orbigny is a consequence of its internal structure, with the porous lithology situated between two shields made of compact micro-gabbroic rock. In our view, when all of the features present in D'Orbigny are taken into consideration, both data and observations are in conflict with an igneous model for angrite genesis (Kurat et al. 2001a, 2001b, 2003, 2004; Varela et al. 2003). Here we discuss the trace element contents of all major and some minor phases in D'Orbigny and confront the results with the existing genetic models for angritic rocks.

### The Igneous Model: Evidence For and Against

Angrites are widely believed to be igneous rocks of basaltic composition originating from a differentiated

Table 2. Ion microprobe analyses (in ppm) of mineral phases in D'Orbigny plate.

Element	Ol. plate GB1	Error	Ol. plate GA2	Error	Ol. Plate GA5	Error	Ol. Ca-rich M	Error
Li	11.8	0.1	8	0.2	6	0.13		
Be	<0.0008		0.0032	0.0007				
B	0.02	0.004	0.022	0.007	0.01	0.004		
Mg	207814	140	195570	253	199375	218		
Si	186800	120	186800	230	186800	200		
P	454	3	220	4	138	2.5		
K	3.5	0.1	2.7	0.2	0.86	0.09	180	3.3
Ca	9368	73	11570	150	9500	116		
Sc	25.6	0.2	24.5	0.4	21	0.3	30	0.84
Ti	183	1	170	2	146	2	588	15.7
V	49	0.4	42	0.6	31.6	0.5	26	1
Cr	543	1.5	515	3	482.5	2.5	149	2.8
Mn	5255	6	5238	11	5284	9		
Fe	457990	350	457328	669	461875	570		
Co	256	2	242	3	232.5	2.5	123	4.5
Rb	0.77	0.15	<0.77		0.58	0.24		
Sr	0.31	0.02	3.5	0.2	0.06	0.012	18	1.2
Y	0.59	0.03	0.8	0.05	0.59	0.05	13.5	0.77
Zr	0.22	0.02	0.19	0.02	0.11	0.01		
Nb	0.03	0.005	0.021	0.007	0.0075	0.0025	0.34	0.17
Ba	0.28	0.03	0.46	0.05	0.041	0.008	27	0.78
La	0.005	0.001	0.056	0.008			0.42	0.083
Ce	0.035	0.006	0.044	0.007	0.01	0.0025	1.27	0.16
Pr	0.002	0.0009	0.012	0.003	<0.0044		0.14	0.05
Nd	0.02	0.003	0.065	0.01	<0.0046		0.84	0.13
Sm	0.01	0.004	<0.022		0.01	0.005	0.78	0.18
Eu	<0.0027		0.015	0.004			0.35	0.1
Gd	0.012	0.004	<0.02		0.011	0.004	1.08	0.27
Tb	0.005	0.001	<0.0068		0.007	0.002	0.27	0.08
Dy	0.049	0.004	0.08	0.01	0.059	0.008	2.43	0.22
Ho	0.019	0.003	0.016	0.005	0.014	0.003	0.57	0.1
Er	0.077	0.006	0.106	0.013	0.09	0.01	1.73	0.2
Tm	0.012	0.002	0.015	0.004	0.0125	0.003	0.34	0.08
Yb	0.176	0.012	0.195	0.025	0.175	0.025	2.83	0.27
Lu	0.031	0.004	0.036	0.008	0.03	0.0075	0.36	0.1



Table 2. *Continued.* Ion microprobe analyses (in ppm) of mineral phases in D'Orbigny plate.

Element	Ol. Ca-rich GAI	Error	Plag. plate GBI	Error	Plag. plate GAI	Error	Sp. megacryst	Error
Li	12	0.2	6.3	0.14	15	0.2	0.87	0.055
Be	0.055	0.005	0.062	0.007	0.065	0.005	0.048	0.004
B	0.16	0.02	0.0165	0.005	0.0062	0.0024	0.0136	0.0037
Mg	187600	200	880	4	1008	4	71880	820
Si	186800	183	204300	194	204300	175	1611	18
P	387	4	62	2	35	1	6.9	0.6
K	14.6	0.3	2.7	0.15	3	0.14	0.47	0.07
Ca	18520	170	95762	156	94560	142	860	
Sc	35	0.4	2.6	0.2	2.2	0.2	4.5	0.3
Ti	1475	4	51	1	54	0.9	1417	17
V	68	0.6	5.5	0.2	4.7	0.11	1867	22
Cr	542	2	1.5	0.1	1.6	0.11	59840	690
Mn	5200	8.5	98	1	106	0.9	1166	14
Fe	456080	530	2742	39	2606	34	178000	2060
Co	225	2	6.3	0.4	6.9	0.4	152	3
Rb	2	0.6					0.66	0.11
Sr	9	0.26	135	1	128	1	0.57	0.07
Y	4.8	0.17	0.12	0.01	0.09	0.01	0.18	0.02
Zr	17	0.5	<0.028		0.026	0.009	0.68	0.07
Nb	1.07	0.09					0.09	0.015
Ba	4.4	0.25	6.3	0.3	5.9	0.3	0.155	0.03
La	0.8	0.065	0.097	0.015	0.061	0.009	0.028	0.007
Ce	2.2	0.14	0.175	0.018	0.168	0.022	0.072	0.015
Pr	0.37	0.03	0.021	0.004	0.015	0.003	0.0088	0.0025
Nd	1.63	0.08	0.083	0.01	0.0755	0.009	0.046	0.009
Sm	0.42	0.05	0.017	0.008	<0.012	0.02	0.018	0.008
Eu	0.14	0.014	0.39	0.03	0.34		<0.0046	
Gd	0.5	0.08	0.026	0.008	<0.015		<0.022	
Tb	0.085	0.01	0.0063	0.0019	0.005	0.002	<0.0055	
Dy	0.9	0.055	0.016	0.004	0.0175	0.0044	0.025	0.006
Ho	0.18	0.02	<0.0033		0.0033	0.001	0.0052	0.0024
Er	0.63	0.04	0.0097	0.004	<0.008		0.016	0.005
Tm	0.095	0.01					<0.003	
Yb	0.63	0.06	<0.015		<0.014		<0.017	
Lu	0.117	0.016	<0.003					

Table 3. Ion microprobe analysis (in ppm) of mineral phases in D'Orbigny.

Element	Aug. core GA4	Error	Aug. core	Error	Aug. rim	Error	Ulvöspinel	Error	Kirsch.	Error	Ti-Fe silicate	Error
Li	2.9	0.06										
Be	0.053	0.0045										
B	0.116	0.012										
P	157	2										
K	3.4	0.1	0.44	0.07	9.75	0.36	1.7	0.36	18.3	0.57	96	2
Sc	190	0.5	252	1.01	20	0.32	6.7	0.44	11	0.27	9.3	0.385
Ti	9042	8	6930	22.7	27770	50.2	1250000	819	1410	13	32400	97
V	368	1	443	1.71	7.42	0.24	298	3.76	0.48	0.07	3.7	0.31
Cr	410	1.3	661	2.53	2.99	0.19	0.83	0.24	2.9	0.22	0.5	0.137
Mn	1572	3										
Co	56	0.8	23	0.82	44.5	1.25	151	5.59	93	2.1	33	1.93
Rb	1.5	0.6										
Sr	22	0.35	21	0.53	88	1.19	1.5	0.378	6.6	0.38	271	3.7
Y	22	0.2	18	0.38	60	0.77	1.8	0.325	19	0.5	102	1.8
Zr	135	0.9	67	1.18	344	2.95	426	7.96	1.4	0.216	865	8.4
Nb	0.63	0.04	0.18	0.062	2.07	0.23	212	5.71	<0.16		197	4
Ba	1.6	0.1	0.06	0.019	1.06	0.07	0.8	0.16	1.68	0.107	30	0.7
La	1.2	0.06	0.77	0.048	5.09	0.136			0.07	0.018	17.4	0.45
Ce	4.3	0.2	0.32	0.108	17.7	0.274	0.28	0.09	0.37	0.047	56	0.87
Pr	0.9	0.05	0.85	0.052	3.49	0.115	0.19	0.07	0.06	0.019	9.9	0.35
Nd	4.9	0.2	4.83	0.128	19.8	0.289	0.35	0.1	0.59	0.06	50	0.84
Sm	1.9	0.12	2.18	0.12	7.78	0.25	0.68	0.17	0.27	0.057	17.4	0.69
Eu	0.47	0.03	0.62	0.045	2.44	0.1	<0.1		0.14	0.03	6.14	0.28
Gd	2.5	0.2	2.32	0.25	8.69	0.486	<0.61		0.9	0.17	19.5	1.13
Tb	0.48	0.05	0.51	0.05	1.62	0.09			0.24	0.04	3.49	0.264
Dy	3.4	0.1	2.32	0.11	11	0.24	0.24	0.09	2.57	0.13	24	0.637
Ho	0.7	0.05	0.66	0.048	2.36	0.09	0.16	0.07	0.72	0.06	5	0.26
Er	2.2	0.1	1.68	0.09	7.31	0.202	0.5	0.136	2.7	0.14	14	0.51
Tm	0.34	0.03	0.24	0.03	1.29	0.08	0.17	0.07	0.59	0.06	2.23	0.186
Yb	2.2	0.1	0.21	0.11	10.6	0.26	0.57	0.156	4.4	0.19	9.6	0.5
Lu	0.4	0.04	0.3	0.046	1.56	0.1			0.62	0.076	1.11	0.19

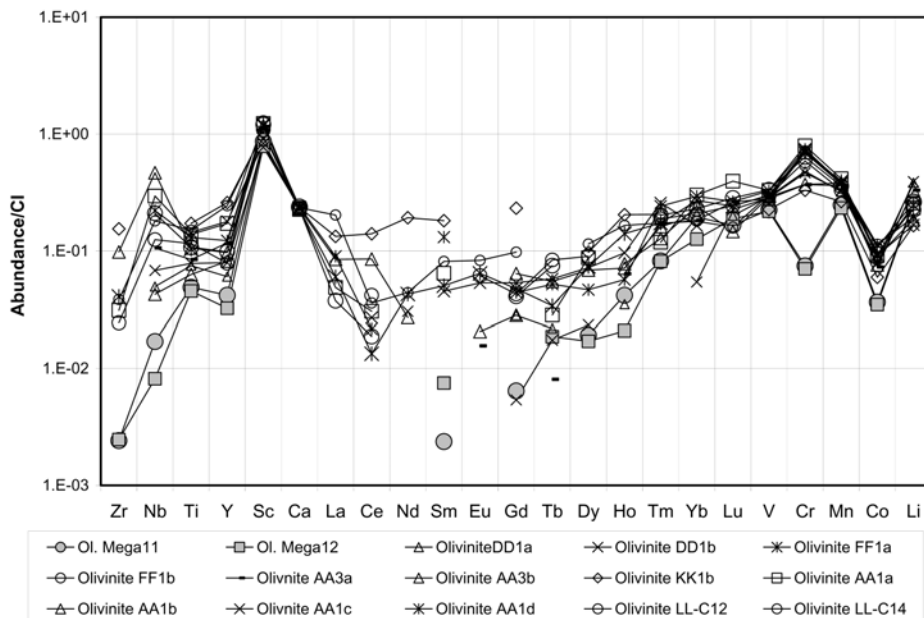


Fig. 5. CI-normalized (Lodders and Fegley 1998) abundances of major and trace elements in olivine megacryst and olivinites. In this and the following figures, elements are arranged in order of increasing volatility, except the REE, which are arranged in order of increasing Z. Note the high content of Cr in olivinites compared to that in olivine megacrysts.

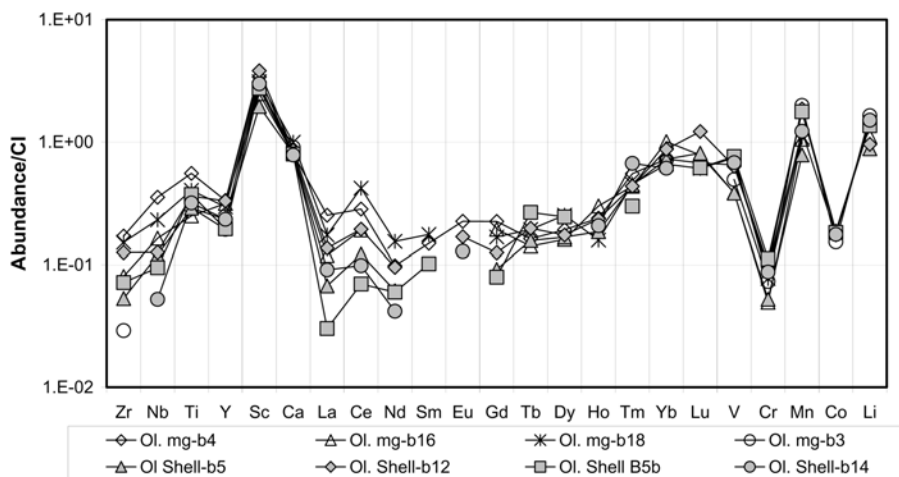


Fig. 6. CI-normalized abundances of major and trace elements in olivine from a hollow shell (Ol. shell) and from the rock with micro-gabbroic texture (Ol. mg.).

planetesimal (e.g., Treiman 1989; Mittlefehldt and Lindstrom 1990; Longhi 1999; Mittlefehldt et al. 2002). Four of the angrites (LEW 87051, Asuka-881371, Sahara 99555, D'Orbigny) seem to be closely related, as the trace element contents of clinopyroxenes and olivines suggest that they all crystallized from similar magmas (Floss et al. 2003). The large variations in incompatible trace element concentrations in phases of LEW 87051, Asuka-881371, Sahara 99555, and D'Orbigny are believed to indicate rapid crystallization under near-closed-system conditions (Floss et al. 2003). This is also in agreement with the petrographic observations, as textures

of all these meteorites seem to be the result of rapid crystallization process (McKay et al. 1990, Mikouchi et al. 1996, 2000; Mikouchi and McKay 2001; Mittlefehldt et al. 2002). However, this is not the case for D'Orbigny. An igneous rapid crystallization model fails when all features of D'Orbigny are taken into consideration (Kurat et al. 2004). The variety of glasses contained in this rock and their occurrence are also inconsistent with the igneous model. Chemical data as well as petrographic observations exclude formation of D'Orbigny glasses by shock or a partial melting process (Varela et al. 2003). Bulk REE abundances and the

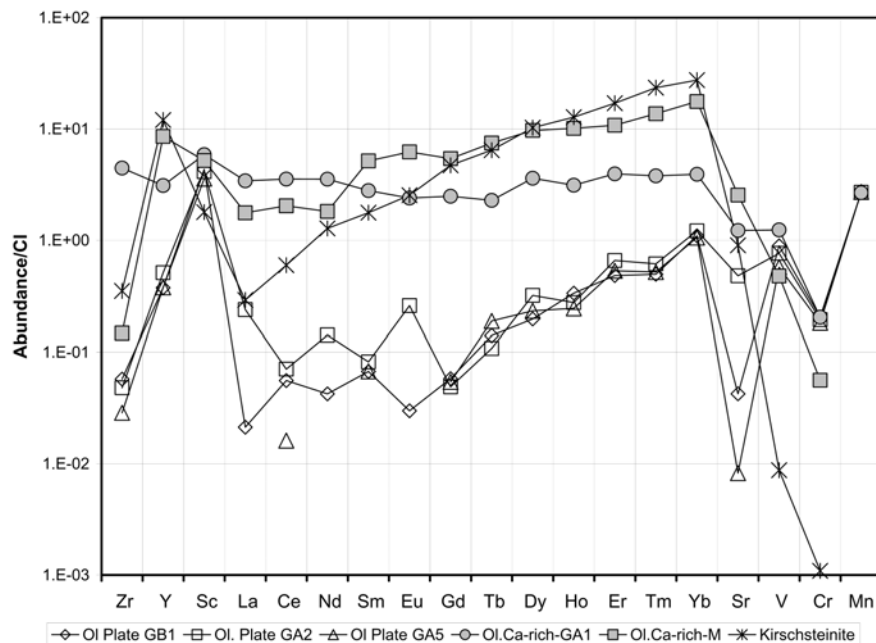


Fig. 7. CI-normalized abundances of major and trace elements in olivine from a plate (GA1-GA2 and GA5), Ca-rich olivines and kirschsteinite. Note the increase in trace element contents ( $\sim 20$ – $100\times$ ) from the early (olivines from the plate) and late (Ca-rich olivine and kirschsteinite) olivines and the deficits in V and Cr in kirschsteinite.

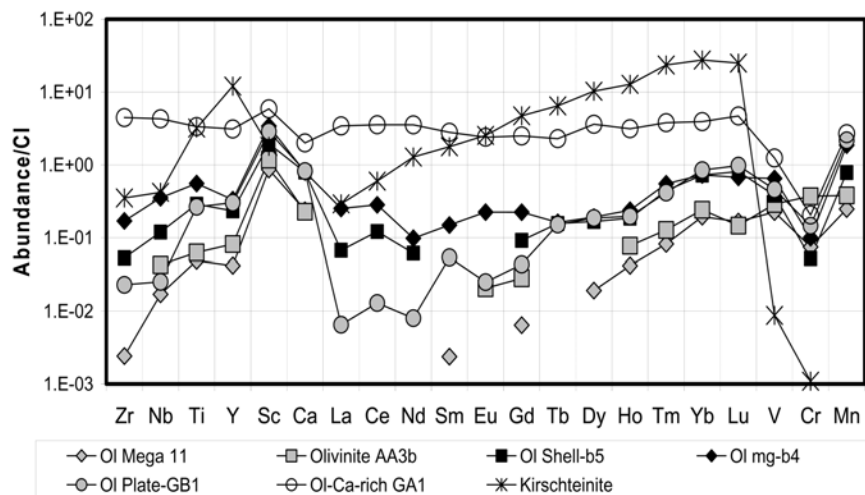


Fig. 8. CI-normalized abundances of major and trace elements in selected olivines from D'Orbigny. Note the variation in trace elements from early olivines (gray symbols), olivines from the shells and mega-gabbroic textured rock (black symbols), and late olivines (open symbols).

compositions of the melt calculated to be in equilibrium with the major phases present another conflict with the igneous formation model (Kurat et al. 2001b, 2003; Floss et al. 2003). The partition coefficient ( $D$ ) for clinopyroxenes and anorthite, calculated with the assumption that the angrites crystallized from a melt with the REE abundances of their bulk composition, turn out to be 1.5 to 4.5 times higher than the experimental  $D$  values of McKay et al. (1994). Floss et al. (2003) attributed these misfits to kinetic effects due to rapid crystallization, which, according to Kennedy et al. (1993) can result in non-equilibrium partitioning of REEs.

Chromium and V are present in olivines in highly variable amounts, as, for example, in olivinites with normalized abundances from  $0.3$  to  $0.8 \times \text{CI}$ . As crystallization proceeds in an igneous setting, we expect olivines to become richer in incompatible elements (e.g., Ti and Y) and poorer in compatible elements (e.g., Cr and V). This is indeed what has been observed by Floss et al. (2003) in several angrites where Ti and Y contents increase and Cr and V decrease with increasing Fe# of olivines. However, what we see in our data is quite different. Abundances in olivines of all four elements, Ti, Y, Cr, and V, increase with

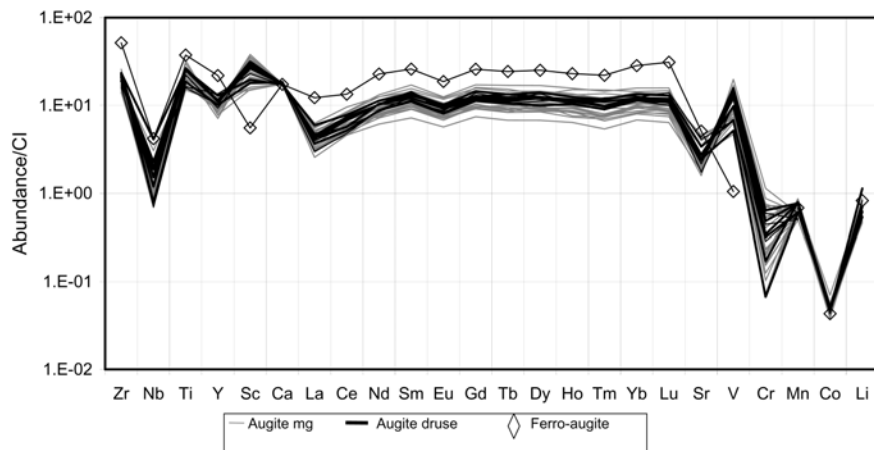


Fig. 9. CI-normalized abundances of major and trace elements in augite from the druses, from the rock with micro-gabbroic texture, and in aluminous hedenbergite (ferro-augite). Trace element contents of both augites overlap. The pattern of the late aluminous hedenbergite follows those of augites but with higher abundances, except for the negative anomalies in Sc and V.

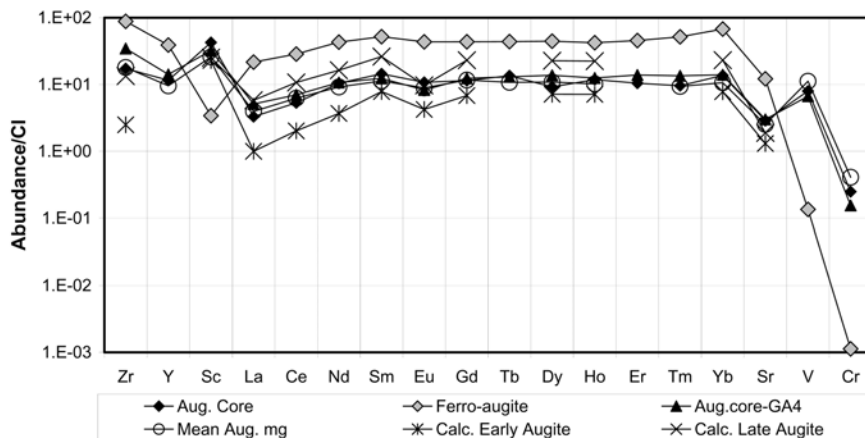


Fig. 10. CI-normalized abundances of major and trace elements in augite cores (aug. core) from druses, a mean value from the augites of the rock with micro-gabbroic texture (mean aug. mg), aluminous hedenbergite (ferro-augite), and the calculated early and late augite composition (calc. early augite, calc. late augite) obtained from modeling D'Orbigny crystallization. The aluminous hedenbergite is enriched in TEs about 10 times with respect to the augite core. Note the relatively low abundances of Sc, V, and Cr.

the Ca content (Figs. 13a, 13b, and 13c), except for Cr in olivinites. The Ca content in olivines can also be taken as a proxy for the time of formation, as the system becomes rich in Ca late in its evolution (e.g., all late phases are extremely Ca-rich, like kirschsteinite). These results clearly preclude crystallization of all olivines from a common melt and suggest instead that Cr and V must have been added to the system during the late stage of rock formation.

### Modeling the Crystallization of D'Orbigny

We model the crystallization of D'Orbigny from a melt having the composition of the bulk rock following the procedure of Ariskin et al. (1997) and using the experimental data on crystallization of angrite melts obtained by McKay et al. (1988). Model calculations were carried out for 1 atm.

pressure and an oxygen fugacity of 1 log unit above the iron-wüstite buffer, in agreement with McKay et al. (1994). Under these conditions, we found a crystallization sequence where anorthite is the liquidus phase and crystallization proceeds (after 7% of the melt crystallized) with anorthite + olivine, followed (after >50% of the melt crystallized) by anorthite + olivine + augite. This crystallization sequence differs from that deduced from experimental and petrographic studies of all basaltic angrites, which indicate a sequence of olivine, followed by plagioclase, and finally pyroxene (McKay et al. 1991; Longhi 1999; Mittlefehldt et al. 2002). Textures of all basaltic angrites commonly suggest olivine to be the liquidus phase. Eliminating these olivines by classifying them as xenocrysts puts anorthite onto the liquidus. As indicated by Kurat et al. (2004) the crystallization sequences for angrites can be deduced from their textures but are model-dependent,

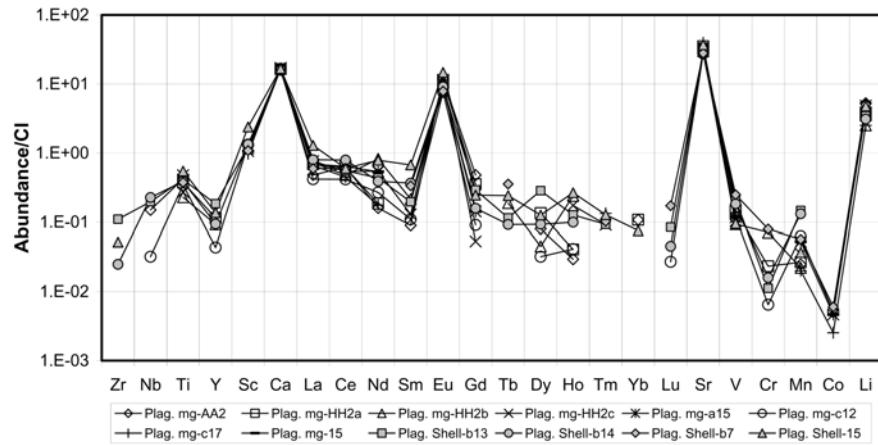


Fig. 11. CI-normalized abundances of major and trace elements in plagioclase from the hollow shell and from the rock with micro-gabbroic texture.

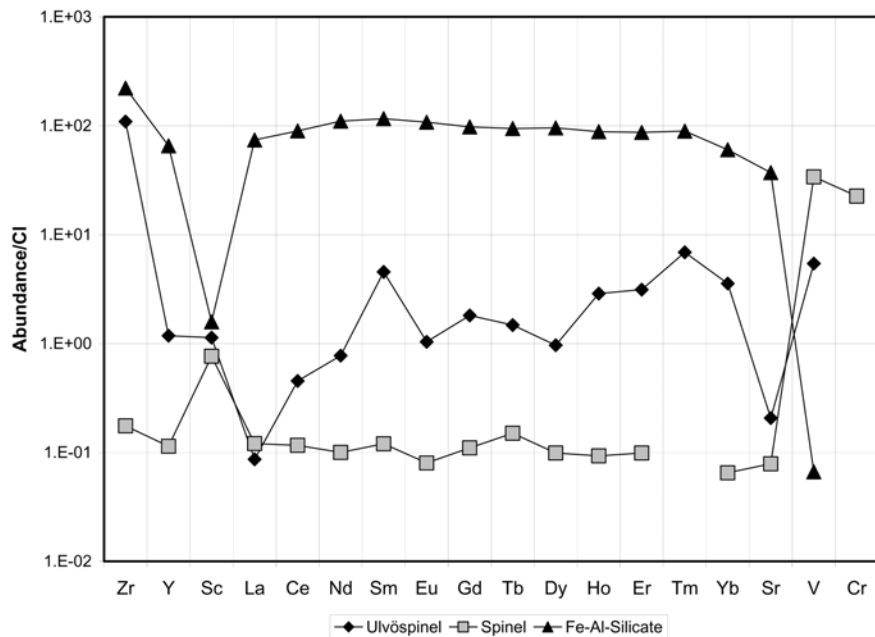


Fig. 12. CI-normalized abundances of trace elements in minor phases: ulvöspinel, a large Cr-bearing Al spinel from the compact micro-gabbroic rock and the Fe-Al-Ca-Ti silicate.

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 shown by the texture is anorthite + olivine, followed by anorthite + olivine + augite, followed by anorthite + olivine + augite + ulvöspinel. The sequence obtained from modeling crystallization of D'Orbigny from its bulk chemical composition (Kurat et al. 2001c) is only shown by LEW 86010, which has abundant large anorthite grains set into a granular matrix but has no igneous texture (e.g., Delaney and Sutton 1988; Mittlefehldt et al. 1998; Mikouchi et al. 2000; Kurat et al. 2004).

If all phases of D'Orbigny crystallized from the same

system, as the igneous model implies, then this relationship should be visible in the distribution of trace elements between the phases. For example, because anorthite, one of the earliest phases to form, takes up large quantities of Eu and Sr (e.g., McKay et al. 1994) and augite did not form before most of the anorthite and olivine had crystallized (~50% crystallization before the appearance of augite; see above), augite should have pronounced negative Eu and Sr abundance anomalies. The olivines from the plate and Al spinel, both of which are contemporaneous with the anorthite of the plate, as well as the early augite (augite cores) do indeed show an abundance deficit in Sr (also probably due to low mineral/melt partition coefficients) and a very small one in Eu (Fig. 14). However,

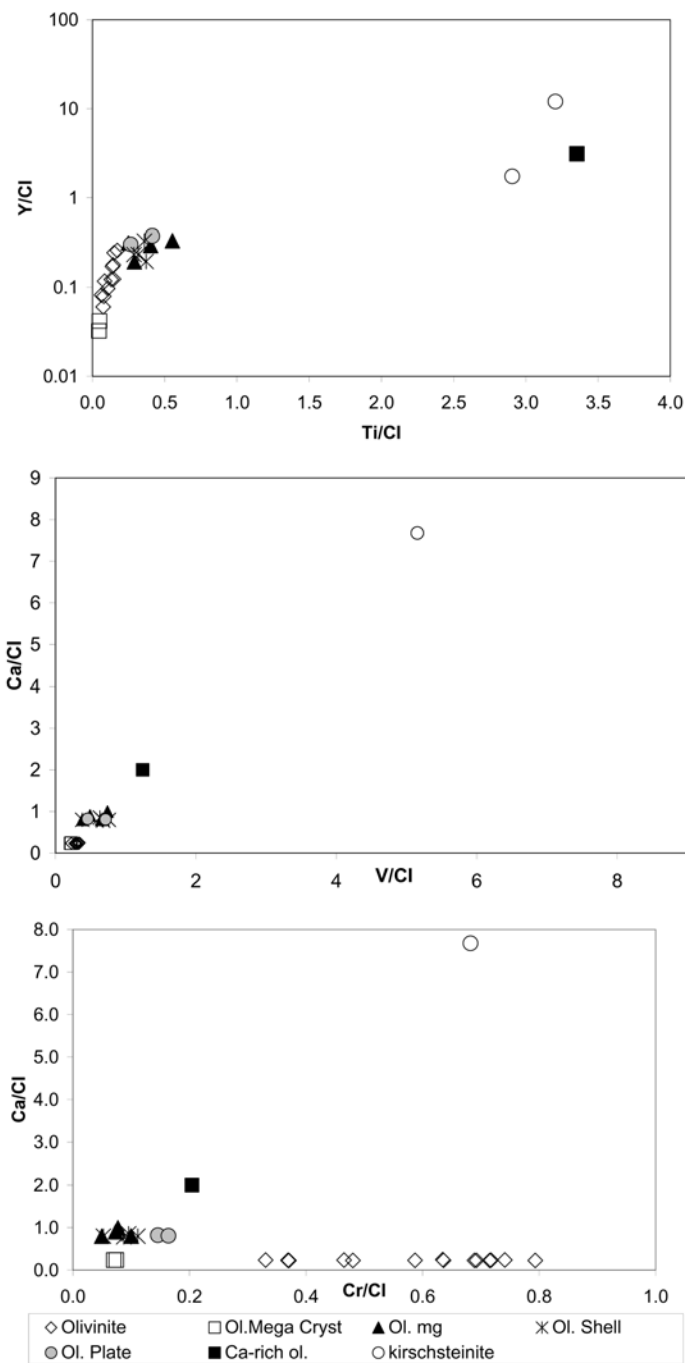


Fig. 13. Compositional variation diagrams of CI-normalized trace and major element abundances in olivines from D'Orbigny: a) Y/CI versus Ti/CI; b) Ca/CI versus V/CI; c) Ca/CI versus Cr/CI.

none of the late phases such as aluminous hedenbergite, Ca-rich olivine, kirschsteinite, and Fe-Ti-Ca-Al silicate show any sign of an underabundance of Eu with respect to the other REEs (Fig. 15). Consequently, they cannot have formed from the bulk system's residual melt.

A serious problem is also posed by Sc, which is mainly carried by pyroxene and olivine. Early olivines and the augite cores are enriched in Sc compared to other trace elements, a

fact that fits the predictions of igneous models. Modeling of trace element evolution as outlined above shows that the residual liquid after crystallization of most of the anorthite, olivine, and augite should be slightly enriched in Sc ( $15.7 \times \text{CI}$ ) over the initial liquid ( $\text{Sc} = 7.7 \times \text{CI}$ ) (Fig. 16, Table 4). Consequently, all late phases should be slightly richer in Sc than the early ones, or at least have comparable contents. The calculated augite composition after crystallization of 50% and

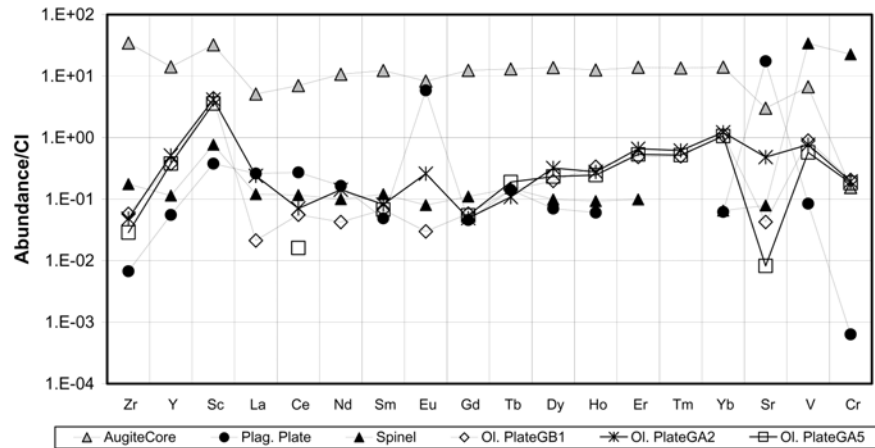


Fig. 14. CI-normalized abundances of trace elements in early phases: plagioclase, Cr-bearing Al spinel, and olivines (GB1, GA2, and GA5) and the augite core.

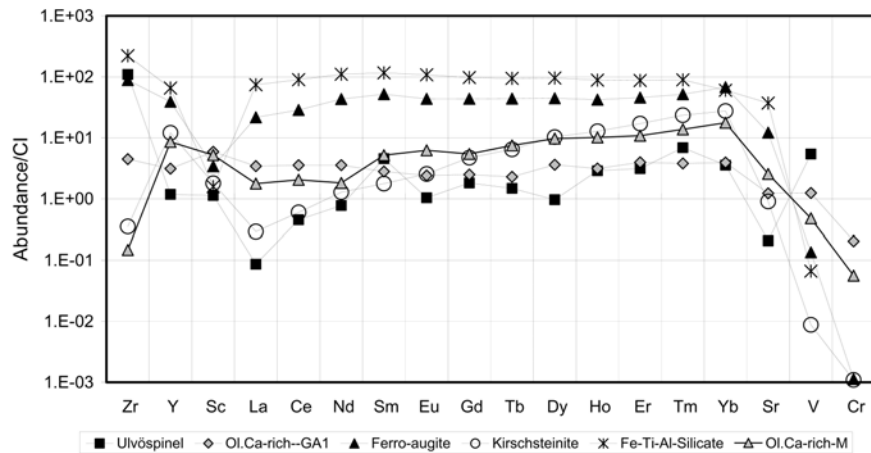


Fig. 15. CI-normalized abundances of trace elements in late phases: ulvöspinel, olivine-Ca-rich (GA1 and M), kirschsteinite, aluminous hedenbergite (ferro-augite), and the Fe-Al-Ca-Ti silicate.

93% of the system (Cal. Early augite and Cal. Late augite in Fig. 10) clearly shows that Sc should have an abundance comparable to that found in the early phases. What we see in D'Orbigny, however, is that the late aluminous hedenbergite is very poor in Sc ( $\sim 5 \times \text{CI}$  compared to  $\sim 50 \times \text{CI}$  for HREEs, Figs. 10 and 15), indicating that either its mineral/melt partition coefficient for Sc is much smaller than that of augite or it crystallized from a system poor in Sc.

A comparison of elemental abundances and phase/melt distribution coefficients (Green et al. 1994; McKay 1986; McKay et al. 1994; Bindeman et al. 1998) reveals that the contents of highly incompatible elements in all phases are far out of equilibrium with a melt of the composition of bulk D'Orbigny and also of an evolved liquid (Table 4). The abundances of the compatible elements in olivine megacrysts, olivinites, olivines from the plate and the Ca-rich olivines are in reasonable agreement with the predictions of the crystallization model (Fig. 17). Abundances of highly

incompatible elements in all olivines, including the megacrysts, however, indicate non-equilibrium with the bulk rock and suggest liquids very rich in these elements ( $>10,000 \times \text{CI}$ ), much richer than any fractional crystallization could possibly produce. Plagioclase from the plate, however, shows very good agreement for the incompatible elements but suggests equilibrium with liquids poor in Ti, Lu, Sc, Mn, and Cr and richer in V, as compared to the bulk rock (Fig. 17, Table 4). Furthermore, the calculated augite composition in equilibrium with an evolved melt is about 0.3 times poorer in REE and up to 0.10 times poorer in HFSE than the augite in the rock (Kurat et al. 2001). Evidently, not only the early phases document an environment very different from that recorded by the late phases, but the two contemporaneous phases (e.g., olivine and plagioclase that form the plate), seem to require liquids of different composition. These data clearly add another serious problem to the many conflicts that have been noticed previously (e.g., Prinz et al. 1977, 1988; McKay



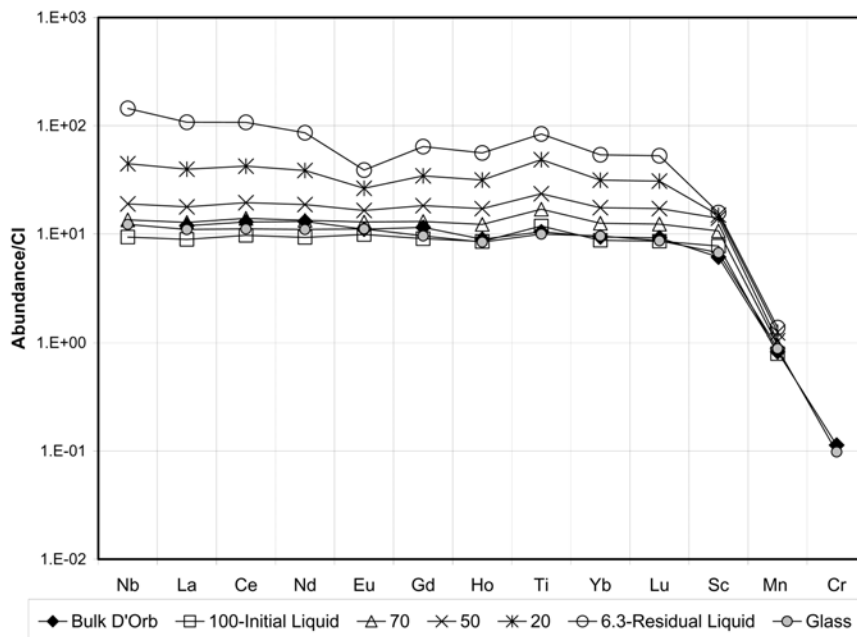


Fig. 16. CI-normalized abundances of trace elements in the bulk D'Orbigny, the glass, and the liquids (100 = initial liquid; 80 = after 20% crystallization; 50 = after 50% crystallization; 20 = after 80% crystallization; 6.3 = residual melt) obtained by modeling the crystallization of D'Orbigny following the procedure of Ariskin et al. (1997).

Table 4. Equilibrium liquid composition.

	La	Ce	Eu	Gd	Yb	Sc	Mn
Glass <sup>a</sup>	10.2	10.7	11.6	9.7	8.9	5.7	0.9
Initial liquid <sup>b</sup>	<b>8.9</b>	<b>9.7</b>	<b>9.9</b>	<b>9.0</b>	<b>8.7</b>	<b>7.7</b>	<b>0.8</b>
Liquid 50% crystallization <sup>b</sup>	<b>17.8</b>	<b>19.4</b>	<b>16.5</b>	<b>18.3</b>	<b>17.5</b>	<b>14.0</b>	<b>1.0</b>
Plag. plate: (abundance/CI)/Kd <sup>c</sup>	11.9	17.0	11.7	11.4	15.5	1.3	0.3
Augite core: (abundance/CI)/Kd <sup>c</sup>	40.2	38.0	32.1	22.3	30.6		
Olivine plate: (abundance/CI)/Kd <sup>d</sup>	425.5	1116.1	40.0	56.9	56.7	16.4	4.9
Olivine megacryst: (abundance/CI)/Kd <sup>d</sup>					10.0	3.3	0.4
Residual liquid (94% crystallization) <sup>b</sup>	<b>107.6</b>	<b>107.3</b>	<b>38.9</b>	<b>64.1</b>	<b>53.8</b>	<b>15.7</b>	<b>1.4</b>
Ca-rich olivine: (abundance/CI)/Kd <sup>d</sup>	68580.0	70997.0	1601.2	2443.6	202.4	22.2	4.9
Kirschsteinite: (abundance/CI)/Kd <sup>d</sup>	5830.0	11968.0	1695.9	4627.5	1417.5	6.8	
Augite rim: (abundance/CI)/Kd <sup>c</sup>	264.0	204.0	138.4	84.9	151.2		

<sup>a</sup>Varela et al. (2003).

<sup>b</sup>Ariskin et al. (1997).

<sup>c</sup>McKay et al. (1994).

<sup>d</sup>McKay (1986) and Green (1994).

et al. 1988; Treiman 1989; Jurewicz et al. 1993; Prinz and Weisberg 1995; Longhi 1999; Mittlefehldt et al. 2002) between an igneous model for the origin of angrites and the mineralogical and chemical observations.

### The New Genetic Model

According to the new genetic model (Kurat et al. 2004), 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. In the course of changing redox conditions,

early minerals became unstable and were replaced by stable assemblages. Consequently, the early phases have disappeared, but later ones did compositionally adapt to the changing conditions. The earliest phases still preserved in D'Orbigny are olivine megacrysts, olivinites, and anorthite-olivine (+sp) intergrowths. The now hollow shells are very likely morphological 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. The growth of the earliest phases forming the spheres must have taken place under reducing conditions. The

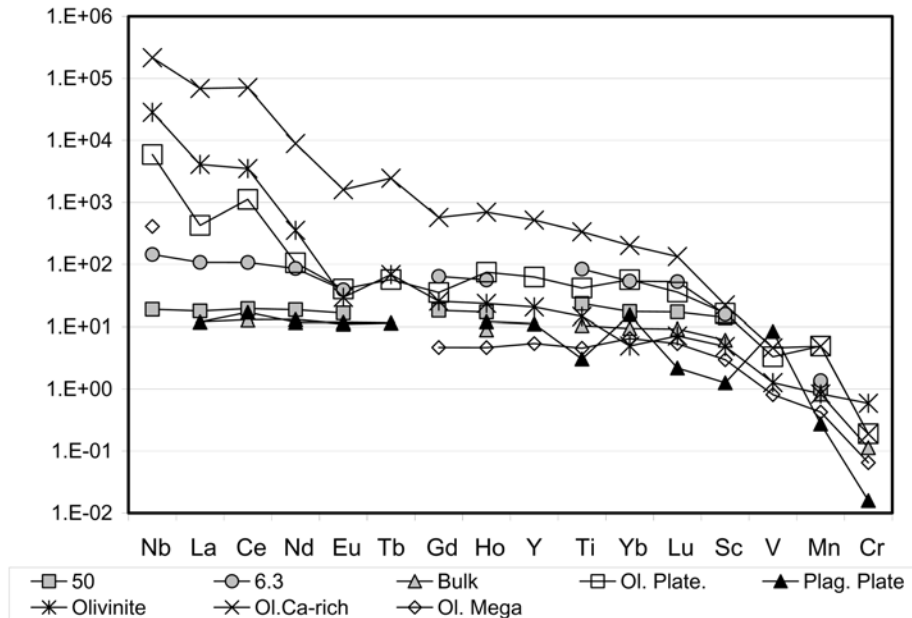


Fig. 17. Comparison of CI-normalized D'Orbigny bulk composition (Bulk) and the calculated liquids (after 50% and ~93% crystallization: 50 and 6.3, respectively) with (CI-normalized abundance)/(phase-melt distribution coefficients) ratios ( $K_d$ s from Green 1994; McKay 1986; McKay et al. 1994; Bindeman et al. 1998).

olivine megacrysts could be relics of these early conditions that, because of their size, survive and were subsequently weakly metasomatized from Fo100 to Fo90. The olivine-anorthite intergrowths covering the spheres must have formed under somewhat less reducing conditions because  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  were available for the formation of spinel. Similar redox conditions are also indicated by the spinel-liquid V partitioning,  $D_V(\text{spinel/melt})$  (Canil 2002). Taking into account the V content of the Cr-bearing Al spinel (1867 ppm, Table 2) and the mean V content of all glasses in D'Orbigny (106 ppm, see Table 2, Varela et al. 2003), the  $D_V(\text{spinel/melt})$  of 17.6 indicates oxygen fugacity of 0.5 log units above the iron-wüstite buffer ( $\sim \text{IW} + 0.5$ , Canil 2002). With increasingly oxidizing conditions, the reduced phase(s) constituting the solid spheres became unstable and vanished in the course of the evolution of the rock. During this event, large quantities of oxidized Fe (plus Mn, Cr, V, and most trace elements) became available in the vapor phase. Olivine began to exchange Mg for Fe, Mn, and Cr, and augites started to grow into open voids and by reaction with olivine. Pigeonite, a phase that should be formed by reaction with olivine is absent, however, suggesting that the physico-chemical conditions prevailing (e.g., low pressure, very high Ca abundance, and temperatures  $\sim 1000$  °C) could prevent its formation and force augite to become stable. A late, highly oxidizing event created the titaniferous aluminous hedenbergite, Ca-rich olivine, and kirschsteinite rims on augites and olivines, respectively.

In the following paragraphs, we explain how the trace element contents of all phases strengthen this genetic model.

The bulk trace element abundances indicate formation of D'Orbigny as a refractory precipitate from a source with chondritic abundances of refractory lithophile elements. The unfractionated abundances of the refractory lithophile elements in the bulk rock (at about  $10 \times \text{CI}$  abundances) indicate derivation from a primitive chondritic source without the need for geochemical processes like partial melting (Kurat et al. 2001, 2004). The relative abundances of all refractory lithophile elements in the glasses are also chondritic, which suggests that the source for the glass had also chondritic relative abundances of the refractory elements. In addition, the abundances of FeO and MnO in the bulk rock and the glasses are similar to those in CI chondrites (Varela et al. 2003; Kurat et al. 2004). The fact that refractory lithophile trace element abundances in olivines are similar to those in olivines from carbonaceous chondrites also points in the same direction. In particular, the unfractionated trace element abundance pattern of the Ca-rich olivine is similar to those of some olivines from carbonaceous chondrites (Kurat et al. 1989; Weinbruch et al. 2000), suggesting that the late metasomatic event likely has been fed by a chondritic source (Fig. 18a).

Olivines from the plate indicate an origin from a melt that was enriched to about  $10 \times \text{CI}$  in Sc, Sr, Nd, and Eu, about  $20\text{--}50 \times \text{CI}$  in the HREE and  $>100 \times \text{CI}$  in La, Ce, and Nb. Because there are no indications that such a melt ever existed in angrite systems (Varela et al. 2003), the REE and Nb are clearly out of equilibrium with the bulk rock composition. Interestingly, the primary trace elements are out of equilibrium while the secondarily introduced elements, Mn

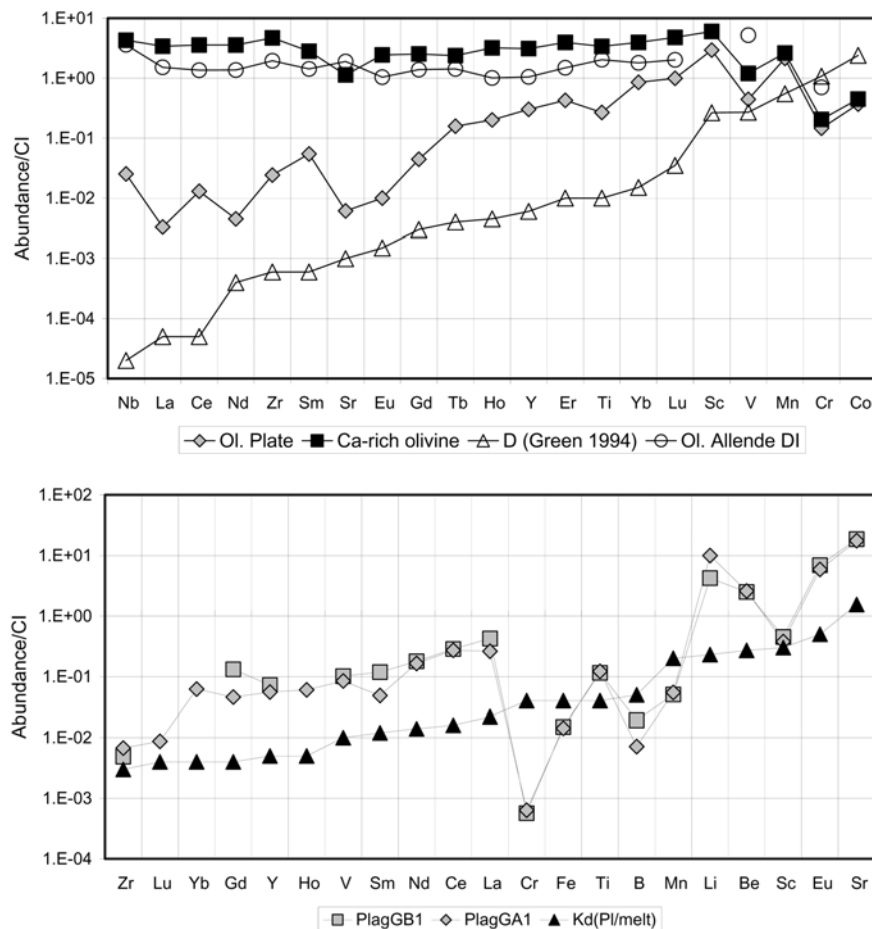


Fig. 18. CI-normalized abundances of trace elements: a) in an early olivine from the plate, in a late Ca-rich olivine, in an olivine from an Allende dark inclusion and the olivine/liquid distribution coefficient ( $K_d$ ) from Green (1994); b) in two early plagioclase grains and the plagioclase/liquid distribution coefficient ( $K_d$ ) from McKay et al. (1994) and Bindeman et al. (1998). The elements are arranged in order of increasing  $K_d$ .

and Cr, are not. This is similar to what has been observed for glasses (Varela et al. 2003). Because the Fe/Mn ratios of the glasses and the rock are close to chondritic, the rock seems to have kept a memory of the source of this metasomatic event. This memory of an unfractionated chondritic source was apparently preserved until the very late phases crystallized (e.g., Ca-rich olivines, ferro-augite, and Fig. 18a).

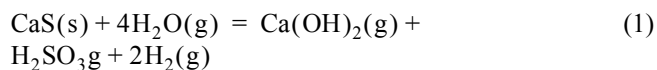
Formation of plagioclase of the plate (one of the earlier phases) must have taken place under reducing conditions (e.g., Eu contents are compatible with a  $K_d$ Eu for redox conditions log IW-1, Fig. 18b). Trace element abundances indicate equilibrium with a source of  $\sim 10 \times$  CI abundances but with large deficits in Cr, Fe, B, and Mn. Obviously, only late phases are rich in Cr, V, Fe, and Mn. This is similar to what can be observed in glass that fills open spaces and that kept its connection with the vapor phase (Varela et al. 2003). Interestingly, the early anorthite also indicates a low supply of Ti, Zr, and Sc. This could indicate that these elements were already deposited into the very early phase(s) forming the spheres. Very late in the history of the rock, Ti and Zr will be

available again (from the breakdown of the early phase[s]) to form ulvöspinel and the Fe-Ca-Ti-Al silicate. Because Sc was separated from Ti and Zr during the subsequent processing of D'Orbigny, the breakdown of the early phase forming the spheres must have resulted in the formation of two phases: a solid, able to keep Ti and Zr until the very late stage, and a vapor, rich in Sc and REE, from which the augites were formed. Olivine data show that Cr and V must have been added to the system during the late stage of rock formation, as was explained above.

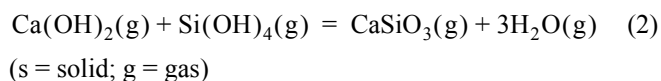
Up to this point of the discussion, we have seen a possible relationship between D'Orbigny and chondrites and have given evidence suggesting that moderately volatile elements (e.g., V, Cr, Mn, Fe) were added by a late metasomatic event. As it is suggested by the new genetic model for angrites (Kurat et al. 2004), large amounts of trace elements could become available in the vapor phase during the late stage of rock formation. If this hypothesis is correct, we must observe substantial trace element abundance variations between the early and late phases.

Late phases are not only enriched in moderately volatile elements with respect to the early phases, suggestive of a metasomatic event, but they also seem to have grown in a different environment. The rock-forming anorthite and the early olivine and Al spinel must have tapped a source that was different from the source of the late phases. Due to the formation of plagioclase, the depletion in Eu and Sr is observed only in the contemporaneous phases such as olivines from the plate, the Al-spinel, and the augite cores (Fig. 14). This feature is absent in the latest phases. None of them show any depletion in Eu with respect to the other REEs. Evidently, the late phases grew in an environment that was rich in trace elements with unfractionated relative abundances. According to Kurat et al. (2004), the trace elements were originally locked up in the earliest phase(s) constituting the spheres. Consequently, early silicate phases indicate normal TE availability ( $\sim 10 \times \text{CI}$ ), except for the highly refractory Zr, Sc, and Ti. The subsequent oxidizing conditions destabilized the TE-rich early phase(s) and TEs were probably liberated by the decomposition of this early phase. Not even the nature of this phase is unknown; what is clearly observed from our data is that there was a sink of TEs and Ca during early rock formation that were afterward available during growth of the late phases. A good candidate that can produce such TE content variations in the system is CaS (Kurat et al. 2004). This phase is not only a major host phase for trace elements under reducing conditions but also it can form spheres (e.g., oldhamite globules in the Bustee aubrite). With changing redox conditions, CaS became unstable and vanished, leaving behind the hollow shells that are very likely morphological copies of solid spheres (Kurat et al. 2004). However, no evidence of the reducing conditions needed to form oldhamite (Lodders and Fegley 1993) seems to have been preserved in the rock, as compared to those indicated by the Eu content of the early plagioclase (e.g., redox conditions log IW-1). Breakdown of CaS under oxidizing conditions can produce perovskite,  $\text{SO}_2$ , and some other mobile chemical species, one of which likely was  $\text{Ca}(\text{OH})_2$ . In this way, large amounts of trace elements and Ca became available in the vapor during growth of the late phases, mainly augite.

One possible way this breakdown could have occurred is:

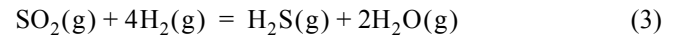


Re-precipitation of Ca into pyroxene could have taken place according to:

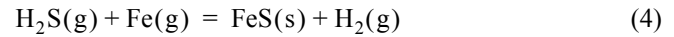


Not even the main part of S was lost to the vapor as  $\text{SO}_2$ (g); we can find some traces of S as sulfides associated with the

very late phases. The liberated S could have re-precipitated forming pyrrhotite:



and



In addition, small amounts of calcite ( $\text{CaCO}_3$ ) are commonly present inside the hollow spheres, which carry a primitive Pb and Sr isotope signature comparable to that of the D'Orbigny bulk rock and the glass (Jotter et al 2002). These could be remnants of the Ca-rich phase constituting the spheres. Furthermore, the calcite also testifies for a strongly oxidizing event that was capable of producing  $\text{CO}_2$ .

It appears that large quantities of Ti and Zr were retained until the very late phases, aluminous hedenbergite, ulvöspinel, and the Fe-Ti-Ca-Al silicate, formed. This suggests that the complete destabilization of perovskite could have happened in the late stage of formation of the rock.

This model, inherently incomplete and imprecise, offers simple and natural explanations for features that are either totally incompatible with or create severe problems for an igneous genetic model of angrites.

## CONCLUSIONS

Given that angrites are widely believed to be igneous rocks, distributions of trace elements were modeled under the assumption that all phases of D'Orbigny crystallized from the same system with the initial composition of bulk D'Orbigny, as the igneous model implies. In such a system, 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. Because anorthite is one of the earliest phases (and takes up most of Eu and Sr) and because augite is formed only after 50% of the melt crystallized, we might expect augite to show a negative anomaly of Eu and Sr. Early augites indeed show small deficits in Eu and Sr as compared to other refractory TEs, but none of the latest phases show any Eu depletion with respect to the other REEs. Obviously, they could not have formed from a melt that had crystallized the major phases of the rock.

Another severe problem is posed by the behavior of Sc. Modeling of D'Orbigny crystallization shows that this element should be present in comparable amounts in early and late phases. The underabundance of Sc observed in late phases suggests that either late aluminous hedenbergite has a mineral/melt partition coefficient for Sc that is much smaller than that of augite or that it crystallized from a system poor in Sc. Furthermore, the results of modeling the crystallization of D'Orbigny do not match those that are expected from an igneous model, as olivines and anorthite that form plates—

two contemporaneous phases—and also the early augites are apparently in equilibrium with different liquids. In addition, the increment in the contents of Cr and V in late olivines, as well as the abundances of highly incompatible elements in all olivines, indicate disequilibrium with the bulk rock and are inconsistent with an igneous origin of D'Orbigny.

The genesis of D'Orbigny rather appears to be more akin to that of chondritic constituents like CAIs than to that of planetary differentiated rocks. The unfractionated abundances of the refractory lithophile elements in the bulk rock (at about  $10 \times$  CI abundances) indicate formation from a primitive chondritic source without any geochemical processes like partial melting. Only the anorthite from the plates retained some memory of the early conditions, which were reducing ( $\sim \log IW-1$ ). During metasomatic introduction of the moderately volatile elements, conditions were somewhat more oxidizing ( $\sim \log IW + 0.5$ ) and became strongly oxidizing in the end (presence of magnetite and ulvöspinel). The oxidizing conditions could have led to a breakdown of the early phase(s) (possibly CaS). This breakdown must have been an incongruent one, giving rise to the formation of two phases: a vapor, rich in Sc and REEs (from which the augites grew), and a solid phase, which retained Ti and Zr until the late stage. The addition of these elements to the reservoir (from which the late Ti-Zr-rich phases grew) could have been provided by the destabilization of its host phase triggered by further increasing oxidizing conditions that characterized the late stage of angrite formation.

Thus, distributions of trace elements document successive events taking place under changing redox conditions that were responsible for the variable distribution of refractory, incompatible elements. The unfractionated trace element abundance pattern of late phases (e.g., Ca-rich olivine with abundances similar to those observed in olivines from carbonaceous chondrites), as well as the high concentration of moderately volatile elements (e.g., Mn, Fe, and Cr) in late phases in chondritic ratios suggest the presence of a late metasomatic event that conferred to the whole rock the elemental signature of its chondritic source.

In conclusion, D'Orbigny records changing redox conditions very similar to those recorded by chondritic constituents but with initial and final conditions (reducing and oxidizing, respectively) being more extreme.

One of the questions that arises is whether we can extend the conclusions drawn for D'Orbigny to all other angrites. This is unknown. Because D'Orbigny is particular and unique, it could turn out to be an exception among all other angrites, or it could turn out to be the first that was able to retain a memory of a large variety of conditions prevailing during formation of angrites. Only the study of more angritic meteorites can give us the correct answer.

**Acknowledgments**—We thank Mike Tubrett and Gabor Dobosi, Memorial University, St. John's, for help with the

LA-ICP-MS. We are grateful to Elmar Gröner for his assistance with the ion microprobe analyses at MPI für Chemie, Mainz. Constructive reviews by Christine Floss and the associated editor Urs Krähenbühl helped to improve this manuscript. Financial support was received from FWF (P-13975-GEO) and the Friederike und Oskar Ermann-Fonds, Austria, NASA grant NAG 5-9801, and CONICET, and SECYT (PICT 07-08176), Argentina.

Editorial Handling—Dr. Urs Krähenbühl

## REFERENCES

- Ariskin A. A., Petaev M., Borisov A., and Barmina G. S. 1997. METEOMOD: A numerical model for the calculation of melting-crystallization relationships in meteoritic igneous systems. *Meteoritics & Planetary Science* 32:123–133.
- Bindeman I. N., Davis A., and Drake M. 1998. Ion microprobe study of plagioclase-basalt partition experiments at natural concentration levels of trace elements. *Geochimica et Cosmochimica Acta* 62:1175–1193.
- Bischoff A., Clayton R. N., Markl G., Mayeda T. K., Palme H., Schultz L., Srinivasan G., Weber H. W., Weckwerth G., and Wolf D. 2000. Mineralogy, chemistry, noble gases, and oxygen- and magnesium-isotopic compositions of the angrite Sahara 99555 (abstract). *Meteoritics & Planetary Science* 35:A27.
- Canil D. 2002. Vanadium in peridotites, mantle redox, and tectonic environments: Archean to present. *Earth and Planetary Science Letters* 195:75–90.
- Delaney J. S. and Sutton S. R. 1988. Lewis Cliff 86010, an ADORable Antarctic (abstract). 19th Lunar and Planetary Science Conference. pp. 265–266.
- Floss C., Crozaz G., and Mikouchi T. 2000. Sahara 99555: Trace element composition and relationship to Antarctic angrites (abstract). *Meteoritics & Planetary Science* 35:A53.
- Floss C., Crozaz G., McKay G., Mikouchi T., and Killgore M. 2003. Petrogenesis of angrites. *Geochimica et Cosmochimica Acta* 67:4775–4789.
- Goodrich C. A. 1988. Petrology of the unique achondrite LEW 86010 (abstract). 19th Lunar and Planetary Science Conference. pp. 399–400.
- Green T. H. 1994. Experimental studies of trace element partitioning applicable to igneous petrogenesis—Sedona 16 years later. *Chemical Geology* 117:1–36.
- Jagoutz E., Jotter R., Varela M. E., Zartman R., Kurat G., and Lugmair G. W. 2002. Pb-U-Th isotopic evolution of the D'Orbigny angrite (abstract #1043). 32nd Lunar and Planetary Science Conference. CD-ROM.
- Jotter R., Jagoutz E., Varela M. E., Zartmann R., and Kurat G. 2002. Pb isotopes in glass and carbonate of the D'Orbigny angrite (abstract). *Meteoritics & Planetary Science* 37:A73.
- Jurewicz A. J. G., Mittlefehldt D. W., and Jones J. H. 1993. Experimental partial melting of the Allende (CV) and Murchison (CM) chondrites and the origin of asteroidal basalts. *Geochimica et Cosmochimica Acta* 57:2123–2139.
- Kennedy A. K., Lofgren G. E., and Wasserburg G. J. 1993. An experimental study of trace element partitioning between olivine, orthopyroxene and melt in chondrules: Equilibrium values and kinetics effects. *Earth and Planetary Science Letters* 115:177–195.
- Kurat G. 1988. Primitive meteorites: An attempt towards unification. *Philosophical Transactions of the Royal Society A* 325:459–482.

- Kurat G., Zinner E., and Palme H. 1989. Primitive olivines with high trace element contents in Allende-AF aggregates (abstract). *Meteoritics* 24:290.
- Kurat G., Brandstätter F., Clayton R., Nazarov M. A., Palme H., Schultz L., Varela M. E., Waesch E., Weber H. W., and Weckwerth G. 2001a. D'Orbigny: A new and unusual angrite (abstract # 1753). 32nd Lunar and Planetary Science Conference. CD-ROM.
- Kurat G., Ntaflos T., Brandstätter F., Varela M. E., Sylvester P. J., and Nazarov M. A. 2001b. Trace element contents of major phases of the D'Orbigny angrite (abstract). *Meteoritics & Planetary Science* 36:A108.
- Kurat G., Zinner E., and Brandstätter F. 2002. A plagioclase-olivine-spinel-magnetite inclusion from Maralinga (CK): Evidence for sequential condensation and solid-gas exchange. *Geochimica et Cosmochimica Acta* 66:2959–2979.
- Kurat G., Varela M. E., Zinner E., and Brandstätter F. 2003. Large plates of anorthite-olivine intergrowths in the D'Orbigny angrite (abstract). *Meteoritics & Planetary Science* 38:A57.
- Kurat G., Varela M. E., Brandstätter F., Weckwerth G., Clayton R. N., Weber H. W., Schultz L., Wäsch E., and Nazarov M. A. 2004. D'Orbigny: A non-igneous angritic achondrite? *Geochimica et Cosmochimica Acta* 68:1901–1921.
- Longhi J. 1999. Phase equilibrium constraints on angrite petrogenesis. *Geochimica et Cosmochimica Acta* 63:573–585.
- Lodders K. and Fegley B. Jr. 1998. *The planetary scientist's companion*. Oxford: Oxford University Press. 371 p.
- Lugmair G. W. and Galer S. J. C. 1992. Age and isotopic relationships among the angrites Lewis Cliff 86010 and Angra dos Reis. *Geochimica et Cosmochimica Acta* 56:1673–1694.
- McKay G., Lindstrom D., Le L., and Yang S. R. 1988. Experimental studies on synthetic LEW 86010 analogs: Petrogenesis of a unique achondrite (abstract). 19th Lunar and Planetary Science Conference. pp. 760–761.
- McKay G., Crozaz G., Wagstaff J., Yang S.-R., and Lundberg L. 1990. A petrographic, electron microprobe and ion probe study of mini-angrite Lewis Cliff 887051 (abstract). 21th Lunar and Planetary Science Conference. pp. 771–772.
- McKay G., Le L., Wagstaff J., and Crozaz G. 1994. Experimental partitioning of rare earth elements and strontium: Constraints on petrogenesis and redox conditions during crystallization of Antarctic angrite Lewis Cliff 86010. *Geochimica et Cosmochimica Acta* 58:2911–2919.
- McKay G. 1986. Crystal/liquid partitioning of REE in basaltic systems: Extreme fractionations of REE in olivine. *Geochimica et Cosmochimica Acta* 50:69–79.
- McKay G., Le L., and Wagstaff J. 1991. Olivines in angrites LEW 87051: Pheno or xenos? (abstract) *Meteoritics* 26:370.
- Mikouchi T., Miyamoto M., and McKay G. 1996. Mineralogy study of angrite Asuka-881371: Its possible relation to angrite LEW 87051. *Proceedings of the NIPR Symposium on Antarctic Meteorites* 9:174–188.
- Mikouchi T., McKay G., and Le L. 2000. A new angrite Sahara 99555: Mineralogical comparison with Angra dos Reis, Lewis Cliff 86010, Lewis Cliff 87051, and Asuka-881371 angrites (abstract). *Antarctic Meteorites* 25:74–76.
- Mikouchi T. and McKay G. 2001. Mineralogical investigation of D'Orbigny: A new angrite showing close affinities to Asuka-881371, Sahara 99555, and Lewis Cliff 87051 (abstract #1876). 32nd Lunar and Planetary Science Conference. CD-ROM.
- Mittlefehldt D. W. and Lindstrom M. M. 1990. Geochemistry and genesis of angrites. *Geochimica et Cosmochimica Acta* 54:3209–3218.
- Mittlefehldt D. W., McCoy T. J., Goodrich C. A., and Kracher A. 1998. Non-chondritic meteorites from asteroidal bodies. In *Planetary materials*, edited by Papike J. J. Washington, D. C.: Mineralogical Society of America. pp. 1–195.
- Mittlefehldt D. W., Killgore M., and Lee M. T. 2001. Petrology and geochemistry of the new angrite D'Orbigny. (abstract #2057). 32nd Lunar and Planetary Science Conference. CD-ROM.
- Mittlefehldt D. W., Killgore M., and Lee M. T. 2002. Petrology and geochemistry of D'Orbigny, geochemistry of Sahara 99555, and the origins of angrites. *Meteoritics & Planetary Science* 37:345–369.
- Pearce N. J. G., Perkins W. T., Westgate J. A., Gorton M. P., Jackson S. E., Neal C. R., and Chenerly S. P. 1997. A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. *Geostandards Newsletter* 21:115–144.
- Prinz M., Keil K., Hlava P. F., Berkley J. L., Gomes C. B., and Curvello W. S. 1977. Studies of Brazilian meteorites III. Origin and history of the Angra dos Reis achondrite. *Earth and Planetary Science Letters* 35:317–330.
- Prinz M., Weisberg M. K., and Nehru C. E. 1988. LEW 86010, a second angrite: Relationship to CAIs and opaque matrix (abstract). 19th Lunar and Planetary Science Conference. pp. 949–950.
- Prinz M., Weisberg M. K., and Nehru C. E. 1990. LEW 87051, a new angrite: Origin in a Ca-Al-enriched planetesimal? (abstract). 21st Lunar and Planetary Science Conference. pp. 979–980.
- Prinz M. and Weisberg M. K. 1995. Asuka-881371 and the angrites: Origin in a heterogeneous, CAI-enriched, differentiated, volatile-depleted body (abstract). *Antarctic Meteorites* 20:207–210.
- Treiman A. H. 1989. An alternate hypothesis for the origin of Angra dos Reis: Porphyry, not cumulate. 19th Lunar and Planetary Science Conference. pp. 443–450.
- Varela M. E., Kurat G., Hoppe P., and Brandstätter F. 2002. Chemistry of glass inclusions in olivines of the CR chondrites Renazzo, Acfer 182, and El Djouf 001. *Geochimica et Cosmochimica Acta* 66:1663–1679.
- Varela M. E., Kurat G., Zinner E., Métrich N., Brandstätter F., Ntaflos T., and Sylvester P. 2003. Glasses in D'Orbigny angrite. *Geochimica et Cosmochimica Acta*, 67:5027–5046.
- Warren P. H. and Davis A. M. 1995. Consortium investigation of the Asuka-881371 angrite: Petrographic, electron microprobe and ion probe observations (abstract). *Antarctic Meteorites* 20:257–260.
- Wasserburg G. J., Tera F., Papanastassiou D. A., and Huneke J. C. 1977. Isotopic and chemical investigation of Angra dos Reis. *Earth and Planetary Science Letters* 35:294–316.
- Weinbruch S., Palme H., and Spettel B. 2000. Refractory forsterite in primitive meteorites: Condensates from the solar nebular? *Meteoritics & Planetary Science* 35:161–171.
- Yanai K. 1994. Angrite Asuka-881371: Preliminary examination of a unique meteorite in the Japanese collection of Antarctic meteorites. *Proceedings of the NIPR Symposium on Antarctic Meteorites* 7:30–41.
- Zinner E. and Crozaz G. 1986. A method for the quantitative measurement of rare earth elements in the ion probe. *International Journal of Mass Spectrometry and Ion Processes* 69:17–38.