

TRACE ELEMENT DISTRIBUTION BETWEEN PHASES OF THE D'ORBIGNY ANGRITE. G. Kurat¹, M. E. Varela², E. Zinner³, P. Hoppe⁴, T. Ntaflos¹ and M. Nazarov⁵, ¹Institut für Geologische Wissenschaften, Universität Wien, Althanstrasse 14, A-1090 Vienna, Austria (gero.kurat@univie.ac.at); ²CONICET-UNS, Dpto Geología, San Juan 670, (8000) B. Blanca, Argentina; ³Laboratory for Space Sciences and Physics Department, Washington University, St. Louis, MO 63130, USA; ⁴Abteilung Kosmochemie, Max-Planck-Institut für Chemie, Postfach 3060, D-55020 Mainz, Germany. ⁵Vernadsky Institute, RAS, 119991 Moscow, Russia.

Introduction: The shape, structure and texture of D'Orbigny and its mineral and bulk chemical compositions indicate a genesis under changing redox conditions, more akin to chondritic than to planetary differentiated rocks. Our data and observations [1, 2] are incompatible with an igneous origin for this rock as entertained by e.g., [3, 4]. Thus, D'Orbigny turns out to be the Rosetta Stone of angritic achondrites. Here we report the results of trace element (TE) studies of major and minor phases which support our previous conclusions.

Results: The TE contents of anorthite, olivine, kirschsteinite, augite, aluminous hedenbergite, spinel, Fe, Ti, Ca, Al - silicate, ulvöspinel and glass were determined by LA-ICP-MS at Memorial University of Newfoundland, following the procedure of [5] and 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 [6].

Results on **glasses** of a variety of occurrences were the subject of a separate report [2]. However, the most abundant glass, which fills voids and hollow shells, has a chemical composition very similar to that of the bulk D'Orbigny. Consequently, its refractory TE abundances are unfractionated and $\sim 10 - 15 \times \text{CI}$, except for Sc, which is slightly less abundant ($\sim 8 \times \text{CI}$).

Olivines have highly variable TE contents. Rare earth element (REE) abundances range from Yb $\sim 0.1 \times \text{CI}$ in olivine megacrysts over Yb $\sim 1 \times \text{CI}$ in olivines from the rock and shells to Yb $\sim 20 \times \text{CI}$ in kirschsteinites. The abundance patterns are all fractionated with La \ll Yb (compare "Kirsch" in Fig. 1). Abundances of other trace elements also vary over wide ranges, e.g., Zr from $\sim 0.002 \times \text{CI}$ to $\sim 0.4 \times \text{CI}$, Cr from $\sim 0.001 \times \text{CI}$ to $\sim 0.8 \times \text{CI}$ and Li from ~ 0.15 to $\sim 12 \times \text{CI}$.

Trace element contents of **augites** vary within very narrow boundaries, except for the aluminous hedenbergite rims. Augite cores are rich in TE, have an almost flat REE pattern at $\sim 10 \times \text{CI}$ with only small negative deviations for La, Ce and Eu (Fig. 1). Contents 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. Aluminous hedenbergite rims have abundance patterns that approximately follow those of the cores but at levels between ~ 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 ($\sim 0.1 - 1 \times \text{CI}$ and $\sim 10 \times \text{CI}$, respectively) and Cr ($\sim 0.001 - 0.03 \times \text{CI}$ and $0.08 - 1 \times \text{CI}$, respectively).

Anorthite is generally poor in TEs with REEs $\sim 0.1 \times \text{CI}$, except for Eu ($\sim 8 \times \text{CI}$), and has a slight La $>$ Yb fractionation (Fig.). Abundances of other TEs 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 TE with a flat REE pattern at $\sim 0.1 \times \text{CI}$ (also Zr), but high contents of Sc ($\sim 1 \times \text{CI}$), V and Cr ($\sim 40 \times \text{CI}$). 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 [1] is very rich in TEs with the REEs and Zr forming a flat pattern at $\sim 100 \times \text{CI}$ (Fig. 1) and Sr slightly depleted ($\sim 40 \times \text{CI}$), Sc depleted ($\sim 2 \times \text{CI}$) and V and Cr strongly depleted (~ 0.09 and $0.0002 \times \text{CI}$, respectively) with respect to the refractory TEs.

Discussion and Conclusion: Our data obtained from D'Orbigny phases are very similar to those that have previously been reported for D'Orbigny [6, 7] and other angrites [4, 8, 9]. Here we would like to discuss our data in the context of the detailed petrography and genetic model provided by [1]. According to this study, the earliest phases still preserved in D'Orbigny are olivine megacrysts, olivinites and anorthite-olivine (+sp) intergrowths. The latter form abundant empty shells, some large plates [11] and a fluffy network throughout the rock. Augites appeared much later in the history of the rock and partly filled the open space between the anorthite-olivine intergrowths' network, leaving some of the space open - the famous druses of D'Orbigny. Very late in the history of the rock, aluminous hedenbergite rims, calcic ferro-olivine and kirschsteinite were precipitated into the interstitial space together with sulfides, abundant ulvöspinel, the unnamed Fe, Ti, Ca, Al-silicate, a silico-phosphate and rare awaruite.

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. For example, because anorthite, one of the earliest phases to form, takes up large quantities of Eu and Sr [12] and augite did not form before most of the anorthite and olivine had crystallized (igneous modeling of the system arrives at $\sim 50\%$ crystallization before the appearance of augite - [13]), the augite should have pronounced negative Eu and Sr abundance anomalies. Early olivine and Al spinel, both contemporaneous with anorthite, and the early augite (augite cores) show indeed an abundance deficit in Sr (also due to low mineral/melt partition coefficients) and a very small one in Eu. However, none of the late phases, aluminous hedenbergite, Ca-olivine, kirschsteinite and Fe, Ti, Ca, Al-silicate shows any sign of an underabundance of Eu with respect to the other REEs. Evidently, the rock-forming anorthite and its companions, early olivine and Al spinel, must have tapped a source that was different from the source of the late ferrous phases in D'Orbigny. According to the model of [1], the late phases grew in an environment that was very rich in TEs, which were liberated by the decomposition of an early phase constituting spheres that were filling the now empty shells. This phase, naturally could not have known of the anorthite, which crystallized much later, and, therefore, did not carry

an anomaly in its Eu abundance. This memory of an unfractionated chondritic source was apparently handed over to the very late crystallizing phases in D'Orbigny.

There are many problems with the distribution of several TEs between the phases in D'Orbigny, notably V and Cr which are present in olivines, for example, in very variable amounts. Such discrepancies are also reported by [4] for D'Orbigny and other angrites and who suggested that kinetic effects during fast crystallization could be the cause.

A severe problem is also presented by Sc which is mainly carried by pyroxenes and olivines. Early olivines and the augite cores are enriched in Sc compared to other TEs – a fact that fits the predictions of igneous models. Crystallization calculations of bulk D'Orbigny following the procedure of [13], however, show that the residual liquid after most of anorthite, olivine and augite had crystallized should be slightly enriched in Sc over the initial liquid. Consequently, all late phases should be slightly richer in Sc than the early ones, or at least have comparable contents. What we see, however, is that the late hedenbergite is very poor in Sc ($\sim 5 \times$ CI compared to $\sim 50 \times$ CI for HREEs), indicating that its mineral/melt partition coefficient for Sc is much smaller than that of augite or that it does not belong to the system. The very low Cr content points into the same direction.

A simple comparison of elemental abundances and phase/melt distribution coefficients of [14] 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. A graphic example is given in Fig. 2 for common olivines in D'Orbigny that suggests pretty good behavior of the compatible elements in early olivines (olivine megacrysts, olivinites, olivines of the shells and anorthite-olivine intergrowths). Abundances of highly incompatible elements in all olivines, including the megacrysts, indicate non-equilibrium with the bulk rock and suggest liquids very rich in these elements ($> 10,000 \times$ CI), much richer than any fractional crystallization could possibly produce. Evidently, the early phases document an environment very different from that recorded by the late phases. A simple igneous origin of D'Orbigny clearly can be ruled out on the basis of these data – as it can be also on the basis of D'Orbigny's structure and texture [1].

In summary, TE data of the phases in D'Orbigny are consistent with the genetic model of [1] that invokes a complex chain of events taking place under changing redox conditions and ending in a metasomatic event under oxidizing conditions and high mobility of refractory, incompatible elements. Similarities between the genesis of D'Orbigny and of CAIs are obvious.

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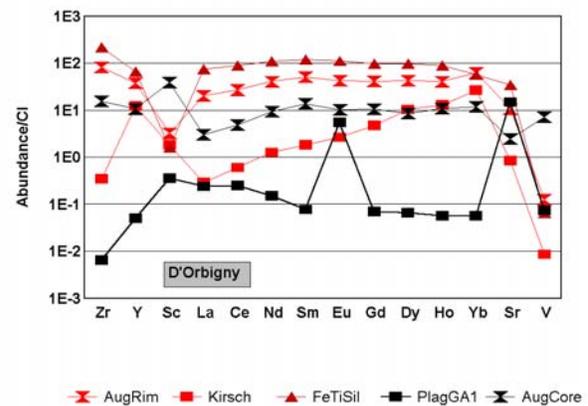


Figure 1: CI-normalized [15] abundances of selected elements in selected phases of D'Orbigny. Early phases are in black, late ones in red.

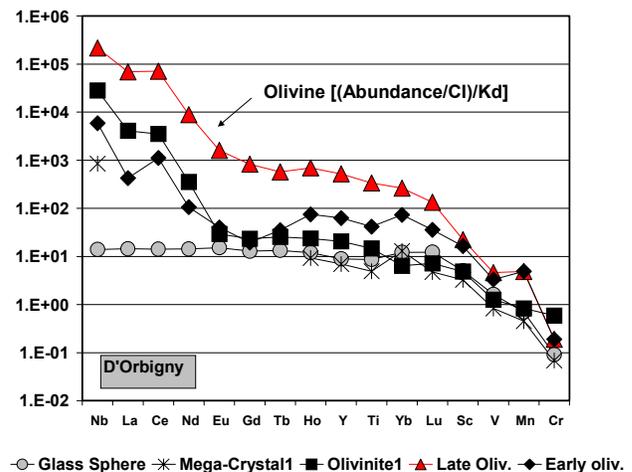


Figure 2: Comparison of CI-normalized D'Orbigny bulk composition (= Glass) with (CI-normalized abundance)/(olivine-melt distribution coefficients) ratios (Kds from [14]). Glass is gray, early phases are in black, late olivine in red.