ISOTOPICALLY HEAVY AND HETEROGENEOUS C IN GRAPHITE OF THE VACA MUERTA MESOSIDERITE.

T. Maruoka[1], M. E. Varela[2], G. Kurat[3], E. Zinner[4], [1]Division of Integrative Environmental Sciences, Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba City, Ibaraki 305-8572, Japan. [2]Complejo Astronómico El Leoncito (CASLEO), Av. España 1512 sur, JS5402DSP, San Juan, Argentina. [3]Institut für Geologische Wissenschaften, Universität Wien, Althanstrasse 14, A-1090 Vienna, Austria. [4]Laboratory for Space Sciences and Physics Department, Washington University, St. Louis, MO 63130, USA

Introduction: The genetic models for mesosiderites are still highly controversial. The most popular model considers mesosiderites as to be a mixture of crustal and core material from a differentiated asteroidal body. Several mechanisms for the silicate-metal mixing – a non-trivial task - have been proposed [1-4] but all are incapable of fully explaining mesosiderite petrographic, geochemical and isotopic features. Consequently, complex scenarios were designed like the proposal that mesosiderites formed by fragmentation and re-accretion of a large (~ 200-400 km diameter) differentiated asteroid [3]. Common to all genetic models proposed is the need to have Fe-Ni metal in a molten state during mixing with the silicate phases [3-5].

Here we report on C-bearing FeNi metal objects and C isotopic ratios of graphite associated with the metal. Our results severely constrain the conditions prevailing during formation of the Vaca Muerta mesosiderite.

Sample and methods: The polished thick section of Vaca Muerta (K) studied (Natural History Museum, Vienna - NHMV) consists of silicate clasts and Fe-Ni metal in about equal proportions. We studied metal-graphite objects by optical microscopy, analytical scanning electron microscopy (NHMV) and electron probe microanalysis (University of Vienna). Carbon isotopic ratios of graphite were measured with the Cameca ims3f ion microprobe at Washington University.

Results and Discussion: Silicate aggregates of Vaca Muerta are preferentially cemented by troilite and metal fills large and small spaces between these aggregates. The void-filling metal areas vary in size from a few µm^2 up to 20 mm^2. Ni contents in kamacite and taenite vary from 4 to 4.9 wt% Ni and 47 to 52.5 wt% Ni, respectively. We can distinguish two types of metal areas: 1) those with fine-grained graphite filigree (from now on referred to as C-rich areas) and 2) those without graphite (Fig 1). In all C-rich areas, graphite distribution is heterogeneous. Grain boundaries between kamacite-kamacite and kamacite-taenite are – or are not – thinly decorated by graphite. Thus, a typical C-rich area has a plessite-like texture with platy to skeletal kamacite as the main phase being covered by a thin mantle of graphite. Crystals are sub parallel to irregularly aggregated with taenite filling most of the interstitial space. C-rich areas are either surrounded by parallel kamacite plates separated by thin taenite plates – resembling Widmanstätten pattern – and covered by a thick graphite mantle or they are covered by a thick graphite mantle only. The space between these objects and the silicate aggregates is mainly filled by kamacite. Graphite decorates only the grain boundaries in the plessite-like aggregates but not in the Widmanstätten pattern-like kamacite-taenite intergrowths. A close inspection of both, graphite inside C-rich areas and in the thick mantles around them, reveals that graphite grew at the expense of the metal, mainly kamacite (Fig. 2). Apparently, graphite is one of the latest phases that was introduced into the Vaca Muerta rock, but only into metal, indicating that metal was a necessary reaction partner. Its distribution is inhomogeneous and obviously governed by the accessibility of the metal at grain boundaries for a reaction with a fluid.

Metal of Vaca Muerta (and other mesosiderites) must have been precipitated at low temperature from a highly mobile medium, as already claimed by [6] a long time ago. In that case, carbonyls could have been at work – like in iron meteorites [7, 8] - and produced kamacite first. Taenite was precipitated after kamacite crystals had aggregated and filled the interstitials between kamacite. Widmanstätten-like kamacite plates with interspersed thin taenite plates could be the result of slow cooling below about 800 °C.

The $\delta^{13}C$ values (rel. to PDB) of graphite in the C-rich areas range from –0.8 ± 1.7 ‰ to +15.3 ± 2.5 ‰ with two extreme values of –5.7 ± 1.3 ‰ and +22.2 ± 1.2 ‰, respectively (Fig. 3). Two measurements in the thick graphite mantle that envelops the C-rich areas show similar $\delta^{13}C$ values: +4.4 ± 1.6 ‰ and +3.0 ± 1.0 ‰, respectively. Carbon isotopic heterogeneity is observed not only among different C-rich areas but also inside a single C-rich area on a micrometer scale.

Carbon isotopic heterogeneity of graphite has previously been reported for the Canyon Diablo and the Campo del Cielo IAB irons [e.g., 8, 9] and for Acapulco and some chondrites [e.g., 10, 11]. These heterogeneities were interpreted as being the result of mixing of carbon from different sources. In the case of the iron meteorites mixing of carbon present in the silicate inclusions and that exsolved from taenite was proposed [e.g., 9] or formation by carbonyl decomposition and subsequent isotopic fractionation between graphite and CO_2 [8]. While the first process requires high temperatures to dissolve carbon in metal, in the second, the metal formed at subsolidus temperature from the very same precursor the graphite formed from. A low temperature formation process for Vaca Muerta metal from a mobile vapor phase is in agreement with the lack of melting of troilite and silicates, the formation and aggregation of early kamacite crystals, the co-precipitation of isotopically heterogeneous graphite, the void-less filling of all spaces (including thin cracks) in the silicates and the unfractionated (roughly chondritic) abundances of siderophile elements in the metal [e.g., 12]. The isotopic heterogeneity in graphite on a micrometer scale indicates that this graphite never experienced a high temperature event. If the graphite in Vaca Muerta is the result of exsolution from the metal (a widely entertained model), the carbon isotopic composition should be homogeneous. The heterogeneous distribution of graphite within a single C-rich zone does not agree with an exsolution process, because both, spatial distribution and isotopic composition should be uniform. The mechanism identified for Campo del Cielo for producing isotopically heterogeneous graphite by carbonyl decomposition and C-CO_2 isotope fractionation [7, 8] is not applicable to Vaca Muerta because its graphite is isotopically heavy – very different from that in iron meteorites and that exsolved from taenite which reportedly has $\delta^{13}C$ values of between –19.7 and –22.1 ‰ [e.g., 9]. Vaca Muerta requires an isotopically heavy C ($\delta^{13}C$ > +22 ‰) source. Possible scenarios could involve C from interstellar molecules [e.g., 13], solar system C that was previously processed through a C-CO_2 fractionation process [e.g., 8] or isotopically heavy C of unknown origin [e.g., carbonates in CCs, 14]. The latter two sources require reduction of CO_2. A possible reaction is:

$CO_2 + H_2$ ==> $CO + H_2O$ (water gas equilibrium) followed by

$5CO + Fe^0$ ==> $Fe(CO)_5$ (carbonyl formation) and

$2CO$ ==> $CO_2 + C$ (Boudouard equilibrium, graphite formation).

The carbonyl formed in this way could have been mobile and have created the space for C precipitation at metal grain boundaries. This process could have taken place at a late stage and only at grain boundaries that were accessible for the CO-rich vapor. Even if the source was isotopically homogeneous this process can produce graphite with varying isotopic compositions by Rayleigh fractionation. This is a new process identified for graphite formation in a solar system rock.

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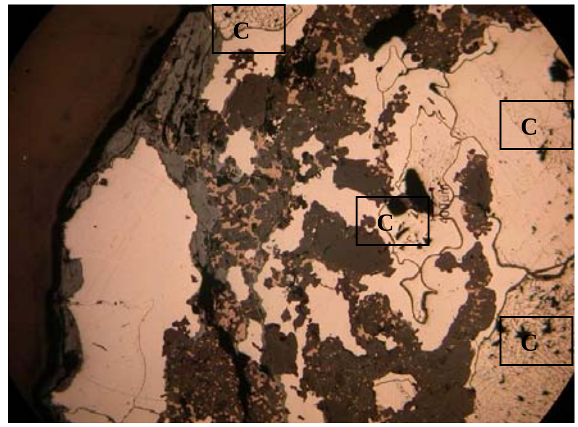

Figure 1: Optical image showing metal (light), troilite (yellow, intergrown with silicates) and silicate (dark) in the polished section of Vaca Muerta (K). C: C-rich area.

Figure 2: Graphite decorating grain boundaries between kamacite grains in Vaca Muerta K2. Note growth of graphite from grain boundary into metal. Optical image, partly crossed polarizers.

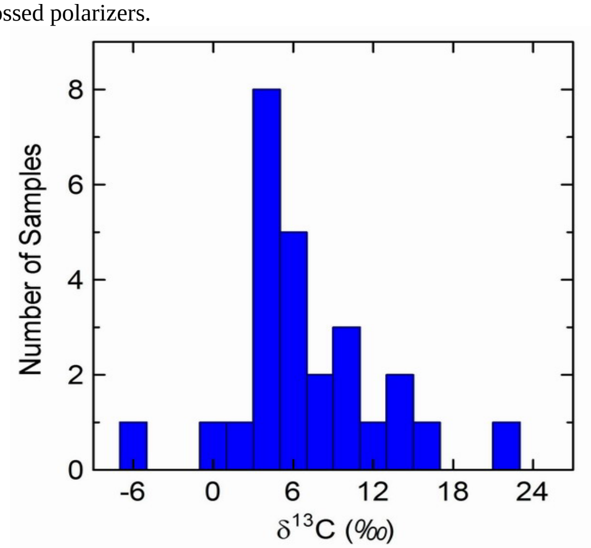

Figure 3: Histogram of $\delta^{13}C$ of graphite in metal of the Vaca Muerta mesosiderite (rel. to PDB in ‰).