A PRELIMINARY MICROANALYSIS OF THE BERKELEY GAS-RICH ALLENDE RESIDUE.
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I - INTRODUCTION - Despite many attempts for identification, the nature of the rare gas-rich mineral phases extracted from the Allende meteorite is still highly controversial. From HNO₃ etching experiments Gros and Anders (1) deduce that most planetary type gases are trapped in a HNO₃-soluble minor phase, labelled "Q" and identified as a mixture of Fe-Ni and Fe-Cr sulfides, whereas the isotopically anomalous xenon component is associated with chromite and carbon. Cerelle et al. (2) also reported the finding of very fine grained chromiferous sulfides around chondrules of the Allende meteorite, that fit the postulated composition of phase Q. In sharp contrast Reynolds et al. (3) consider carbon as the major host phase for both types of components.

We have already reported (4) on a microprobing procedure, which allows to study the successive alteration of a selected micron-sized grain through a complex sequence of treatments, and which combines the use of a high voltage electron microscope (HVEM) equipped with an energy loss analyzer (HVES), an Auger microscope, a scanning electron microscope with its associated energy dispersive X-ray analyzer (SEM + EDX), and an ion probe. The analysis of material with the HVES technique, the Auger microscope, and the ion probe looks very promising. But we realized over the last few years that these techniques, when applied to micron-sized insulator grains, have limitations still to be overcome. Consequently, in the present work we have applied a simplified version of this microprobing procedure, that relies on the use of the HVEM and the SEM + EDX to analyze a colloidal fraction of an (HF, HCl)-etching residue of the Allende meteorite, kindly provided to us by J. Reynolds, and that will be identified as R₁.

Our strategy was then to select about 25 individual representative grains from R₁, to submit these grains to HNO₃-etching and/or vacuum pyrolysis up to 1000°C, and to tentatively correlate the resulting changes in the grains characteristics with the very drastic changes observed upon similar treatments, in both the concentration and the elemental and isotopic composition of the rare gases found in (HF, HCl)-residues, by the Berkeley and the Chicago groups.

II - THE "SIMPLIFIED" MICROPROBING PROCEDURE - Our simplified microprobing procedure has limitations. In particular the effective resolution of the HVEM, obtained by directly observing electron micrographs taken at a magnification of 10,000, is about 50 Å, and that of the EDX chemical analysis is about 4 Å. Fortunately these limitations could be counterbalanced by improving our sample preparation technique. In this technique, based on the use of gold or tungsten electron microscope numbered grids, we first disperse the grains on a collodion film fixed on the grids. Then, the grains are coated with a 200 Å-thick carbon layer and the collodion backing is finally dissolved in isoamylacetate. The grains are thus very firmly fixed in the carbon film and present an uncoated surface. In addition to extensive cleaning in organic solvents, they can be subjected to very harsh treatments, such as those currently used in the rare gas studies of the Berkeley and Chicago groups (etching in fuming HNO₃; stepwise heating up to 1600°C; etc...) without being lost from their support. Any slight shrinking of the grains, that results from such treatments, can be readily detected as the C-film keeps a "print" of the original grain habit. In addition, the good contact between the grains and their conducting substrate greatly reduces any beam charging effects. This interesting feature already very useful for the SEM + EDX runs, will considerably ease the future analysis of the grains with an improved model of the Auger microscope, and particularly intended to detect light elements (C, N, O, P) in the superficial layers of the...
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Grains. Finally the grains firmly stuck to their substrate can be easily reset in the same orientation with respect to the primary electron beam of the HVEM and SEM. As all analytical conditions (beam intensity, grain orientation, SEM scanned area, etc.) can be kept constant through the various analytical steps the reliability of any conclusion dealing with "change" in the grains characteristics is seriously improved.

III - RESULTS

III.1 - Untreated RI-residue. Before the HNO₃-etching, the RI-residue looks as a complex assemblage of micron-sized grain aggregates. These aggregates can be classified in two major types: the C-grains are essentially made of a C-rich amorphous matrix, loaded with numerous tiny crystalline inclusions with size < 500 Å, whereas the Xtal-grains are aggregates of much coarser crystalline grains. A statistics bearing on about 100 individual aggregates randomly chosen suggests that the abundance of the C-grains and Xtal-grains is about 70% and 10% respectively, with the remaining aggregates appearing as a mixture of both types of grains. The X-ray analysis also reveals that weak Fe and Cr lines are present in the spectra of the C-grains whereas the Xtal-grains can be further subdivided as follows: 50% dubbed as (Al, Mg) -grains essentially show strong Al and Mg lines, 25% are chromites and 25% a mixture of chromites and (Al, Mg)-grains. In almost all X-ray spectra of both the C and Xtal-grains lines most likely associated with contamination elements (Cl, K, Ca) were present, whereas S-lines were barely detectable above background. Finally, before thermal annealing we found no evidence for latent and/or etched tracks in the Xtal-grains.

III.2 - Vacuum pyrolysis of RI at 1000°C. The only major change so far detectable with the HVEM is the formation of a high density (5.10 cm⁻²) of tiny crystallites (size < 100 Å) in the (Al, Mg)-grains. The Mg-line of these peculiar grains also notably decreased in intensity upon heating.

III.3 - HNO₃-etching of RI. The (Al, Mg)-grains were completely dissolved during the HNO₃-etching, and consequently the intensity of the Al and Mg lines considerably decreased. In sharp contrast neither the C-rich matrix nor the tiny inclusions characterizing the C-grains looked affected by the HNO₃-etching, and this is further illustrated by the constancy of the Fe and Cr-line intensity after etching.

III.4 - Comparison of grains from RI with meteoritic grains directly handpicked in carbonaceous chondrites: i. Orgueil. Carbon-rich grains from the fine grained matrix of Orgueil were selected by UV-fluorescence optical microscopy. HVEM observations revealed that most of these grains are indeed similar to the C-grains observed in RI, with the exception that they contain a smaller density of tiny crystalline inclusions. The remaining few C-rich grains of Orgueil, which were quite distinct in showing a rounded habit, a fibrous texture and more numerous inclusions, have not been observed in the (HF, HCl)-residues; i.i. Allende. Christophe-Levy found sulfur-rich grains on the external surface of peculiar chondrules of Allende. Our HVEM observation of these grains has convinced us that they are not present in the RI-residue.

IV - DISCUSSION - We encountered three major difficulties in the present study. First some of the characteristics of the RI-grains could be artifacts resulting from the separation procedure applied at Berkeley, and consequently some of our conclusions might be erroneous. Second, the effective HVEM limit of resolution used in our work (~50Å) is not sufficient to detect slight changes in the C-rich matrix of the C-grains. Finally, as samples of the (HF, HCl)-residues prepared by the Chicago group were not available for our study, it is difficult for us to discuss in a meaningful way the results of this group.
The major result of our investigations was to pinpoint the role of the (Al, Mg)-grains of R1, which belong probably to a variety of spinel, and which appear either isolated or embedded in the C-matrix of the C-grains, as a plausible host phase for the rare gases of R1. Indeed these grains are the only ones to be severely affected upon artificial treatments (HNO$_3$-etching and vacuum pyrolysis at 1000°C), known to trigger drastic changes in the rare gas distributions of R1. In particular, the sharp phase transformation triggering the formation of crystallites, could indeed be responsible for the observed "simultaneous" release of rare gases in R1. Also this role of the (Al, Mg)-grains would also agree with the following qualitative prediction: the HVEM runs of our "home-made" (HF, HCl)-residue of Orgueil only show C-grains, similar to those found in R1, but containing a lower density of inclusions. Consequently, if a crystalline component contains the rare gases, we would rather predict that the (HF, HCl)-residue of Orgueil should release less rare gas per g of residue than Allende, and this predicted trend seems compatible with the corresponding experimental observation.

The phase transformation mechanism, responsible for the formation of the crystallites embedded in the (Al, Mg)-grains after heating, has still to be elucidated. However we were struck by the following observations: the TEM-micrographs of a chromite grain extracted from an (HF, HCl)-residue of Allende, and which can be found in the paper of Fraundorf et al. (5), show before heating a high density (5.10$^5$ cm$^{-2}$) of tiny crystallites, that clearly grow upon heating up to 400°C. This crystallite density is strikingly similar to that we observed in (Al, Mg)-grains heated up to 1000°C. Thus we cannot exclude the exciting possibility that a fair proportion of the R1-grains, including chromites and (Al, Mg)-grains, have been homogeneously irradiated in high fluxes of nuclear particles. As suggested by the presence of fossil crystallites in chromite, these tracks could have been subjected to a partial thermal annealing in nature. Although they cannot any longer be observed as latent and/or etched tracks, they would still contribute to enhance the etching rate of the (Al, Mg)-grains in HNO$_3$, in thus explaining the anomalous etching of such "spinel" in HNO$_3$. With this "track-crystallite" hypothesis the track densities observed in the X-tal-grains of R1 would be about 50 times larger than the value of 5.10$^6$ cm$^{-2}$, expected from the fission of a superheavy nuclei and inferred from Xe concentrations (5).

Unfortunately, our basic conclusion concerning the nature of the rare gas host mineral phases in (HF, HCl)-residues of Allende is not compatible with those inferred by both the Berkeley and the Chicago group. Consequently we should further investigate Allende residues prepared at both places, and check with a series of simple experiments the validity of a track origin for the crystallites observed upon heating in crystalline grains from these residues. Then it will be perhaps possible to strongly argue for the presence of a magic component, i.e. the "irradiated-spinel"-grains in a variety of meteoritic mineral separates showing isotopic anomalies, and such as the R1-residue and the refractory white inclusions of Allende.