Allende Whole Rock and CAI Studies: Thermal Equilibration History and Noble Metal (Re)distributions in Mineral Phases*

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Z. Naturforsch. **44a,** 1015–1027 (1989); received June 30, 1989

Dedicated to Heinrich Wänke on the occasion of his 60th birthday

Ru, Os, and Ir in Allende whole rock and coarse grained CAIs are present in amounts up to 80% in phases other than inert Pt-metal alloys. Selective chemical dissolution was used to dissolve sulfides by ascorbic acid-H_2O_2 and metal (NiFe)-silicate-oxides by HF/HCl. Carbon-rich, spinel-chromite residues were left from the demineralization procedures and scavenged inert material such as Pt-metal alloy particles. The Pt-metal contents in sulfide phases from the Allende whole rock sample and the total Pt-metal contents of the CAI samples give near-cosmic to cosmic interelement ratios. Pt-metal ratios in all the other separated phases are fractionated. The Fe/Co ratio in the carbon-rich residue from the CAI and in the sulfide fractions from Allende whole rock and CAI-bulk samples is 230, the same as is reported for sulfides in the Zelda fremdlinge. A scheme for mixing aggregates from different regions of "Allende-space" in the solar nebula is proposed to account for the Pt-metal and Fe-Co distributions observed here.

Chemical alteration processes in condensed material may have required moderate to high temperatures in the nebula to have caused the interelement relationships observed. We determined the final equilibration temperatures to which components of Allende were subjected. Temperatures are based on the distribution of Hg between labile (low T) and retentive (high T) sites in silicate rocks. Compositionally and texturally different CAI clasts and the matrix associated with one of the clasts were equilibrated at 778–975 °C. The averaged thermal equilibration temperature for seven bulk (matrix) Allende samples reported previously was 670 °C. The final thermal equilibrations of the clasts probably occurred before Allende was assembled.

Introduction

Results of a study of Hg, Os, Ru, Ir, Fe, Co, Cr, and Sc, and C, N, and H in carbon-rich and spinel-chromite residues from demineralization of Allende (C3) and Murchison (C2) chondrites have been reported by Jovanovic and Reed [1]. We report here concentration data for most of these elements in Allende whole rock (wr) and Ca-Al-rich inclusions (CAIs) which were subjected to dissolution procedures selective for specific mineral phases. Element distributions were determined in sulfides which are ascorbic acid-H_2O_2 soluble, in metal-silicate-oxides which are HF-HCl soluble, and in acid insoluble residues of carbon and spinel-chromite and co-precipitated inert particles such as refractory metal nuggets.

Most of the research on C2 and C3 chondrites has been dominated by various microprobe studies exploring the mineralogical, chemical, and textural details of CAIs. Since trace elements in submicroscopic phases as well as those measured by microprobe methods are determined in our experiments, the results supplement the microprobe data. Acquisition of whole rock data is essential to understanding the evolution of meteorites. As an example of its importance, Johnson et al. [2] in seeking trace-element-rich relict refractory phases needed to account for the differences in partition coefficients for experimental and natural Type B CAI minerals concluded that trace element carriers unobserved microscopically are required. A whole-rock trace element inventory, therefore, is essential for identifying and assessing the roles of such carriers. Although less discriminating than physical separations, selective chemical dissolution procedures are superior in the sense that microscopic and submicroscopic phases cannot be lost.

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All CAI materials have undergone post-condensation thermal alteration, thus in addition to concentration and element ratio data, we report on the final moderate to high temperatures to which some CAIs were subjected and postulate where this occurred. The temperature measuring technique is based on the distribution of Hg between labile (low temperature) and retentive (high temperature) sites in whole rock samples. For this investigation several types of CAI separates, matrix associated with CAI material, and bulk meteorite were measured.

The report is in three parts. We first describe the unpublished results on Pt-metals in demineralization solutions of sulfide and NiFe-silicate-oxides from Allende and Murchison whole rock studies. The carbon-rich residue data were published [1]. The second part presents the results of an experiment in which bulk meteorite and separated CAI material from Allende were measured in parallel. The third part presents the results of Hg stepwise heating experiments on various CAI samples; these measurements give information on the final equilibration temperatures for the CAI silicates and oxides. The major conclusions from the experiments are that only a fraction of the Pt-metals Os, Ru, and Ir are concentrated as inert alloys in CAIs in Allende, significant amounts are in sulfides and in NiFe-silicate-oxides in CAIs; and that final equilibration temperatures ranged from ~800°–1000 °C.

General Background

Large enrichments of rare gases and Pt-metals are found in Allende carbon-rich residues [3, 4]. Enrichment of Hg has also been established [1].

Pt-metals are found to occur in NiFe phases and/or as discrete Pt-metal alloys in high temperature CAIs in Allende (e.g. [5–10]. Additional data from experiments by Jovanovic and Reed [11] provide direct and indirect evidence that major fractions of the Pt-metals in the bulk meteorites are not associated with metallic phases in high temperature inclusions in Allende and Murchison.

Coarse grained CAIs are composed primarily of high temperature minerals and are considered to be the earliest oxide condensates. Prior to condensation of Ca-Al-Ti oxide phases, refractory noble metals would have condensed and could have served to nucleate oxide condensation. It is postulated that a fraction of Fe-Ni, because of their high partial pressures in the nebula, would have condensed with the noble metals [7]. Presumably, Pt-metals such as Ru, Os, and Ir would have been completely condensed before the major Fe condensation began. Rare earth elements (REEs) and other highly refractory elements would have condensed along with the Ca-Al-rich phases. The Pt-metals and the REEs are not significantly fractionated in bulk coarse-grained inclusions although they are fractionated in the various mineral components. Hence, it is concluded that the minerals condensed in the presence of a gas with cosmic proportions of these elements. The mineralogy and chemistry of CAIs is summarized in Grossman et al. [12]. Both types of refractory elements, oxide forming and noble metals, are enriched by 17.5–20 in CAIs in Allende relative to C1 meteorites [12–16].

Optical descriptions and electron microscopic analyses of a large number of metal-like particles in Allende inclusions published by Fuchs and Blander [17] are relevant to the results reported here. Their analyses indicated that W and Mo, both high temperature condensates as metals, may appear as oxides and oxides and sulfides, respectively. Ru, Os, and Ir are always present as metals. In recent work by Wark [9] on refractory metal nuggets in Type A CAI 3643, two groups of nuggets were noted: one rich in the most refractory metals Re, W, Os, Ir, and Mo and the second rich in Ru, Pt, Rh, Fe, and Ni. Blum et al. [18] note, however, that Ir is the only refractory siderophile abundant in both NiFe and RuOs phases. Sulfide and some oxide and associated metal phases could have formed by secondary reactions of S and O with primary condensates (e.g. [10, 19–21]) or with homogeneous alloys containing NiFe and refractory siderophile elements [18]. The microscopic data provide details of the modes of occurrence of mineral phases and their major and trace element compositions critical to understanding conditions of formation and subsequent alteration histories. The presence of rims and veins of secondary minerals is evidence for alteration (metamorphism/metasomatism) of CAIs [19, 20, 22–24]. However, the microscopic data are not representative of the whole rock since, as noted, refractory trace elements are also in submicroscopic phases. The matrix minerals in Allende have grain sizes from sub-μm to a few μm [14, 25]. In our preliminary report [11] we concluded that either "most Pt-metals in the solar nebula were not early condensates or that sufficiently chemically reactive conditions occurred subsequent to the early condensation to cause noble metals to enter secondary phases".

Related to the distributions and redistributions of noble metals in Allende components are the thermal histories of these components. Wark [19] noted that all CAI-rich materials in Allende have suffered secondary alteration or metasomatism and the part of the temperature history of the nebula after CAI condensation can be deciphered from this alteration. Kurat [26] explored a number of options to explain solar nebula, pre-accretion alteration processes. Some of these occurred at >800 °C; see also Palme and Wark [27]. Haggerty and McMahon [28] postulate oxidation of nebular metal at temperatures from $\lesssim 600°$ to 900 °C depending on the oxygen fugacity. Blum et al. [18] use NiFeRu phase equilibria to arrive at a probable metamorphic temperature of 600 °C. Our measurements address this final thermal history and provide an absolute measure of an equilibration temperature which is either a closure temperature in a cooling system or a maximum prograde metamorphic temperature. Cooling from a melt temperture is apparently ruled out based on Housley and Cirlin's [20] point that magnetite would not be the end product.

Experimental

Part I. The sample preparation and the demineralization procedures have been described [1]. Bulk Allende and Murchison samples were measured. The emphasis in these early experiments had been to measure Hg, Os, Ru, Ir, C, H, N, and Fe, Co, Cr, and Sc in carbon-rich phases separated by demineralization procedures in a manner that assured freedom from accidental trace element contamination. Neutron activation analysis procedures were used. Trace elements in the demineralization solutions are reported here.

Part II. In the follow-up experiment, bulk Allende and separated CAIs were measured and compared. Several coarse-grained-inclusion areas were excavated to yield ~270 mg of Type B inclusions. L. Fuchs of Argonne National Laboratory (ANL) described the inclusion material as being ~99% Type B. Sulfide was also present as is typical for CAIs. The number of areas excavated made this a random sample. Two bulk meteorite chips totaling ~670 mg were crushed and aliquots were used as the whole rock sample. On hindsight, as will be noted below, we believe that these chips and our mixing did not yield representative homogenized samples of CAI or bulk Allende.

The composite CAI sample was crushed and split into two fractions, one was measured directly and the other fraction was subjected to demineralization. The element concentrations in various chemically separated phases were determined. The same procedure was applied to the bulk meteorite sample. We designate the four samples measured as CAI-bulk and CAI-demineralized, and whole rock (wr)-bulk and whole rock (wr)-demineralized.

Sample dissolution is a two step procedure and is described with references in [1]. In the first step, ascorbic acid-H_2O_2 was used with intermittent ultrasonic dispersal over an ~20 hr period to dissolve the sulfide phases. In this reaction, release of sulfide ions does not occur, sulfide is oxidized to sulfate. Precipitation of acid insoluble sulfides such as HgS is avoided. The second step is HF-HCl dissolution of NiFe, silicates and some oxides. In the early study, Part I, the insoluble residue was separated into carbon-rich and spinel-chromite phases by dispersing the carbonaceous material into ethyl and amyl alcohols. In the Part II experiment, this step was dropped. The trace element contents of the combined residue phases were measured. This residue contained the scavenged inert microscopic refractory Pt-metal particles coprecipitated with the carbonaceous material and spinel-chromite.

Thermal neutron activation analysis was used to determine the trace elements measured. Os and Ru were determined after radiochemical separations. Ir, Fe, Co, and Sc were measured instrumentally on aliquots of solutions from which the Os and Ru were to be extracted.

Part III. Hg was measured in several mineralogically and texturally different CAIs by the stepwise heating extraction procedure. Temperature steps were usually 110 or 130, 175, 300, 450, 600, and 1200 or 1300 °C. A thermometer calibrated on the basis of the ratio of Hg released at or below 450 °C to that released at >450 °C up to 1200 or 1300 °C is used to determine temperatures (see [29]). This procedure enables us to determine the temperature at which Hg was finally equilibrated between labile and retentive sites in silicates and oxides. The CAI samples were described by L. Fuchs (ANL) using both microscopic and X-ray techniques. Their characterizations are given in Table 5 in the Results section.

Results

Part I. Initial Allende and Murchison Results

We reported Hg, Os, Ru, and Ir in carbon-rich and inert oxide residues from Allende and Murchison bulk

Table 1. Pt-metals in sulfides (ascorbic acid-H_2O_2) and metal-silicates-oxides (HF, HCl) demineralization solutions and in meteorite whole rock (bulk) samples [a].

Sample	Os ppm	Ru ppm	Ir ppm
Allende, C-4 [b]			
Demineralized sample			
Sulfides	0.03	–	0.14
NiFe-silicate-oxides	–	–	~0
Residue	0.16	–	0.10
Summation	0.19	–	0.24
Bulk Sample	2.5	–	(0.81)
Allende, C-6			
Demineralized sample			
Sulfides	0.43	0.40	0.22
NiFe-silicates-oxides	0.09	1.4	0.44
Residue	0.013	0.010	0.002
Summation	0.53	1.81	0.66
Bulk samples	1.2	0.81	(0.81)
Murchison, C-5			
Demineralized sample			
Sulfides	–	0.35	0.49
NiFe-silicates-oxides	–	0.03	0.05
Residue	0.08	–	0.005
Summation	0.08	0.38	0.55
Bulk sample	0.64	(0.88)	(0.60)

[a] The solutions measured were from a study of Pt-metals, Hg, Fe, Co, Sc, and Cr in carbon-rich and spinel-chromite residues [1]. ( ) = literature concentrations [31]. Literature data for Allende whole rock are Os = 0.93 ppm, Ru = 0.9 ppm, Ir = 0.81 ppm; CM data are used for Murchison, Os = 0.64 ppm, Ru = 0.88 ppm, Ir = 0.60 ppm.

[b] C-4, C-5, and C-6 are experiment numbers. The concentrations are for the total wt of sample used for dissolution procedures. Because of long decay times, Ru was not measured in C-4. It was not possible to measure Pt-metals in all solutions because of the difficulty in recovering carriers from large volumes.

meteorites demineralized by ascorbic acid-H_2O_2 and HF-HCl dissolution of sulfides and NiFe-silicate-oxide phases [1]. Os, Ru, and Ir concentrations measured in some of the demineralizing leach solutions are given in Table 1. The carbon and spinel-chromite residues data from the earlier report are combined in Table 1 and reported per gram of sample. The data are incomplete since the original experiments were not planned for determining trace element concentrations in the leach solutions. However, the leach solutions data indicate that up to 80% of the Pt-metals in bulk meteorite samples were dissolved by the demineralization solutions. In those cases for which we have reasonable data, significant amounts of the leached Pt-metals are in the ascorbic acid-H_2O_2 solution, i.e., in sulfides. Because of the large volumes of solution involved (liters) and the possibility of loss by oxidation, recovery of Os was low and fewer Os data are available. The concentrations of Pt-metals in the ascorbic acid-H_2O_2 solution are significant since noble metal alloys, if present, should be not be attacked by such a weak acid solution.

The state of disaggregation of the sample being demineralized was important. Allende in the C-4 experiment contained coarse material and was difficult to demineralize with HF-HCl. The coarseness of the sample may have prevented the ascorbic acid-H_2O_2 solution from gaining access to occluded sulfide phases, although major sulfide phases pentlandite and pyrrohitite could have been dissolved.

The C-6 Allende sample was a sieved fine grained (< 100 μm) fraction from lightly crushing chunks of meteorite. The coarser material (~ 100 μm – 1 mm) was used for the C-4 experiment. Samples were deliberately not crushed to fine grain size and homogenized because of contamination concerns. The fine material may be representative of the matrix. This could explain the much lower, 0.013 and 0.002 ppm, Os and Ir in the residue in C-6 than the 0.16 and 0.10 ppm Os and Ir in C-4, Table 1. The C-4 sample could have contained more CAI material. Note that Blum et al. [18] detected no discrete siderophile-element-rich phases in Allende matrix. A problem with some of the concentration data (C-6, Table 1; CAI, Table 3) is the lack of agreement between the sums of the separated fractions and the literature (C-6) and Aliquot (CAI, Table 3) bulk rock data. Sample homogeneity could be a factor for the 0.1 – 1 gm used. This problem is discussed further in Part II c) where the data set is complete and hence where material balance considerations of how Pt-metals are distributed are feasible.

Part II: Comparative Results on Allende Bulk and Ca-Al-rich Inclusion Samples

a) Fe, Co, Sc Concentration Data

The data discussed here are for the 670 mg whole rock Allende sample which was crushed and split into wr-bulk and wr-demineralized samples and for the 270 mg of randomly excavated Type B CAI material which was crushed and split into CAI-bulk and CAI-

Table 2. Concentrations of Sc, Fe, Co, and Fe/Co ratios in Allende whole rock and CAI samples *.

Sample	Sc ppm	Fe wt%	Co ppm	Fe/Co
Whole rock				
Demineralization sample				
Sulfides [a]	2.7	5.5	241	228
NiFe-silicates-oxides [a]	12	6.7	46	1460
Residue	0.06	(299 ppm)	3.3	91
Summation	15	12	290	410
Bulk sample	20	19	519	387
Literature [b]	12.7	23.6	610	370
CAI				
Demineralization sample				
Sulfides [a]	1.2	0.64	23	233
NiFe-silicates-oxides [a]	45	0.07	8.2	86
Residue	0.3	(817 ppm)	3.7	223
Summation	46	0.71	40	178
Bulk sample	37	0.27	11	236
Literature [c]	127.3			

* Counting statistical errors are $\leq 20\%$.

[a] Demineralization solutions: ascorbic acid-H_2O_2 for sulfides, aqueous HF-HCl for NiFe-silicates-oxides.

[b] Mason [31].

[c] Grossman and Ganapathy [16].

demineralized samples. The concentrations of Fe, Co, and Sc in wr-bulk and wr-demineralized Allende differ on the average by ~60%, Table 2. The Fe and Co concentrations in the wr-bulk sample are within 20 and 15%, respectively, of the mean literature values. This agreement justified the use of literature Os, Ru, and Ir concentrations of Allende to calculate concentrations of these elements in the sulfides, the acid soluble fraction, and the residues from the samples studied. In the earlier experiments (Part I) Os and Ru monitors were irradiated with the samples and were used to calculate concentrations. Reproducibility of the Pt-metal concentration data is discussed in Section c).

In the wr-demineralized sample, most (80%) of the Sc is in the HF-HCl soluble fraction; this is expected since Sc is predominantly in silicates. Similar amounts of Fe occur in sulfide (5.5 wt%) and in olivine (6.7 wt%) which is the Fe bearing silicate mineral in the meteorite. The Co is concentrated (83%) in sulfide phases which are troilite and pentlandite [30].

In the CAI-bulk sample, Sc is enriched by a factor ~2 over the wr-bulk sample; whereas Fe and Co are depleted by factors of ~71 and ~45, respectively. The Sc in the CAI-bulk sample and in the summed components of the CAI-demineralized sample agree to within 20%. Fe and Co, on the other hand, exhibit larger variations; they are in minor phases not uniformly distributed in CAI. Both elements are concentrated in the sulfide phase in the CAI. Wark (private communication) finds an average of 0.58% Fe (we find 0.64%) and 0.03% S in CAIs. If all the sulfur is present as FeS this would represent only 0.05% Fe.

It is necessary to consider whether the sulfide in the CAI represents matrix contamination. Based on the sulfide data, ~13% matrix is necessary to account for the CAI sulfide content. Only 1% of the amount of metal-silicate-oxide in the matrix is present in the CAI. Extremely selective contamination would be required, i.e., by sulfide but not other matrix material. Furthermore, CAI sulfides contain ~1/2 the Sc found in the wr sample sulfides. This amount of Sc does not seem to be reconcilable with ~13% matrix sulfide based on Fe in wr- and CAI-sulfide separates in the CAI material unless CAI sulfides contain much higher Sc than matrix sulfides. It is possible that in CAI, an Fe (and Sc) bearing phase other than sulfide is dissolved by ascorbic acid-H_2O_2. As discussed in section b) below, Fe/Co ratios in NiFe-silicate-oxides and Pt-metal ratios (section d)) in sulfide and NiFe-silicate-oxides in CAI and bulk meteorite samples also are not consistent with matrix contamination of the CAI material. We conclude that the CAI material studied was essentially matrix free; hence, the results represent the CAI material alone.

b) Fe, Co Concentration Ratio Considerations

The Fe/Co ratios are significant. These are constant at ~230 in wr and CAI ascorbic acid-H_2O_2 soluble (sulfide) phases, in the CAI demineralization residue, and in the CAI-bulk sample, Table 2. Ninety percent of the Fe in the CAI is in ascorbic acid-H_2O_2 soluble phases. The Fe/Co ratios in HF-HCl solutions for the whole-rock and CAI are 1460 and 86, respectively. The wr carbon-rich residue has an Fe/Co ratio of 91. These are very different from the ~230 ratio. If contamination of the CAI material by matrix sulfide is invoked to account for the CAI sulfide Fe/Co ratio of 230, this must have occurred naturally (i.e., not a laboratory artifact) since the other components of the matrix (HF-HCl soluble fractions and carbon-rich residues) which also should contaminate the CAI material, have Fe/Co ratios that are very different from the ratios in the corresponding CAI fractions.

Armstrong et al. [10] report on sulfides in the Zelda fremdlinge. Fremdlinge are present as complex aggregates of metal grains, sulfides, phosphates, oxides, and silicates in Allende coarse-grained CAIs. Zelda has about equal modal percentages of pyrrhotite and pentlandite. The former has an Fe/Co wt ratio of 236, the latter of 31.4. It may be coincidental but the Fe/Co ratio of 236 is the same that we find in the sulfide fractions and in the CAI carbon-rich residue. The implication could be that the dominant sulfide is submicroscopic and in both whole rock and CAI it is pyrrhotite, and that some of this sulfide could be occluded in the material residual from acid treatment.

c) Ru, Os, Ir Data

It is necessary to consider whether the trace element data to be discussed are compromised by vagaries in the experimental procedures. Duplication of sampling is not possible on the < gram sample size scale. Nevertheless, the number of cases of reproducibility of data from different Allende samples suggests that the experimental procedure is not a problem. Examples are sulfide data from the C-6 bulk sample (Table 1) and the whole rock sample (Table 3) with 0.43 and 0.30 ppm Os and 0.22 and 0.21 ppm Ir, respectively; the summations of Os fractions for these samples also agree at 0.52 and 0.51 ppm, respectively; and the sum of fractions for Ir in C-4 (Table 1) and whole rock (Table 3) are 0.24 and 0.34 ppm, respectively. In addition, C-6 (Table 1) bulk sample with 1.2 ppm Os and 0.81 ppm Ru agree reasonably well with literature values of 0.93 and 0.9 ppm, respectively. It appears that sampling alone accounts for any lack of agreement between samples.

Both CAI-bulk and -demineralized samples are enriched in Pt-metals by ~ 5–10 times over the whole rock samples, Table 3. This is within the range of values for a number of individual inclusions reported by Grossman et al. [12]. The relatively lower concentrations of Pt-metals in the whole-rock Allende sample used for demineralization are consistent with the Fe and Co data and indicate that the Allende sample used for demineralizations was relatively depleted in the Pt-metal and Fe-Co bearing phases. The Pt-metals in the CAI-bulk sample are higher than in the CAI sample used for demineralization; however, Fe and Co are relatively enriched in the latter. Sampling of minor and trace phases appears to be a major problem. Sampling of major phases is less erratic; Sc, for instance, which represents the silicate phases in the CAI, is in reasonable agreement for the CAI-bulk and -demineralized samples.

The sulfide phases (Table 3) in the wr-demineralized sample contain 35–50% of the Pt-metals; most of the remainder 20–40% is in the carbon- and spinel-chromite-rich residue. About 47% of Ru and Ir but only ~ 7% of the Os are in the CAI-sulfide phase. In the whole-rock sample, only a few percent of the Pt-metals dissolved during the strong acid treatment following removal of sulfide phases; 30–80% of these metals in the CAI are acid soluble.

The CAI sulfides are 3.5 to 5 times enriched in Ru and Ir relative to whole rock sulfides; Os is depleted. A reasonable explanation for the low Os in the CAI sulfide phase is that Os was in a sulfide or some other phase which is either not soluble in ascorbic acid-H_2O_2 or was inaccessible to this reagent. The large amount of Os (80%) in the CAI HF-HCl soluble fraction is unexpected since Os is not in NiFe particles which are acid soluble but is reported to be in OsRu nuggets. Possibly these are not inert to acid. In the CAI-demineralized sample, all three elements are enriched in the strong, acid-soluble fraction compared to the whole rock-demineralized sample. As discussed

Table 3. Concentrations of Os, Ru, and Ir in Allende whole rock and CAI samples*.

Sample	Os ppm	Ru ppm	Ir ppm
Whole rock			
Demineralization sample			
Sulfides [a]	0.30	0.18	0.21
NiFe-silicates-oxides [a]	0.01	0.02	0.03
Residue	0.2	0.05	0.11
Summation	0.51	0.25	0.34
Bulk sample, literature [b]	0.93	0.9	0.81
CAI			
Demineralization sample			
Sulfides [a]	0.13	1.0	0.70
NiFe-silicates-oxides [a]	1.5	0.64	0.62
Residue	0.12	0.46	0.19
Summation	1.7	2.1	1.5
Bulk sample	4.9	3.7	4.7
CAI, literature [c]	7.3	8.2	6.5

* Counting statistical errors are ≦20%.

[a] Demineralization solutions: ascorbic acid-H_2O_2 for sulfides, aqueous HF-HCl for NiFe-silicates-oxides.

[b] Mason [31].

[c] Grossman and Ganapathy [16].

Table 4. Relative abundances of Pt-metals in chemically separated phases in Allende whole rock and CAI samples and in noble-metal-rich particles *.

Phase	Fe %	Ru/Os	Ir/Os	Ru/Ir	Labeled as
Allende (Mason [31])	23.6	0.97	0.87	1.11	cosmic
Allende whole rock (this work)					
Demineralization sample					
Sulfides [a]	5.5	0.60	0.67	0.86	~ cosmic
NiFe-silicates-oxides [a]	6.7	2.0	3.0	0.67	fractionated
Residue		0.25	0.55	0.45	
Summation	12	0.49	0.67	0.74	
Allende CAI (this work)					
Demineralization sample					
Sulfides [a]	0.64	7.8	5.4	1.4	fractionated
NiFe-silicates-oxides [a]	0.07	0.43	0.42	1.0	
Residue		3.8	1.6	2.4	
Summation	0.71	1.2	0.87	1.4	cosmic
Bulk sample	0.27	0.75	0.96	0.78	~ cosmic
Allende bulk CAI (Grossmn and Ganapathy [16])		1.1	0.85	1.3	cosmic
Metal nuggets (Wark and Lovering [5])	(8) 9.9	(4) 1.2	(8) 0.38	(8) 3.0	fractionated
		(5) 2.5	1.64	0.61	
		(1) 0.29	<0.06	>18	
Metal nuggets	(7) 5.1	(7) 0.19	0.63	0.30	fractionated
Whole core (Wark [9])	25	0.28	0.74	0.37	
Metal particles (Blander et al. [8])	4.6	0.13	0.57	0.22	fractionated
Zelda fremdlinge	3.99	0.83	0.18	4.6	fractionated
OsRu metal nuggets (Armstrong et al. [10])	10.04	0.47	0.39	1.2	
Zorba fremdlinge siderophiles (Grossman et al. [32])	39.1	0.34	1.0	0.34	fractionated
Cosmic, C1, C2, C3 (Mason [31])		0.97–1.3	0.84–1.1	1.1–1.5	cosmic

* The phases in which similar fractionated Pt-metal ratios occur are indicated by connecting lines. – ( ) Number of nuggets.
[a] See footnote [a], Table 2.

below the ratios of total Os to Ir are close to cosmic for both CAI-demineralized and CAI-bulk samples, hence the chemical procedures did not cause selective losses.

d) Pt-Metal Concentration Ratios

Ru/Os, Ir/Os, and Ru/Ir ratios for the Allende wr-sulfide sample, the CAI-bulk, and CAI sum-of-demineralization fractions are cosmic or nearly so (Table 4). The summed data for the demineralization fractions for the wr-bulk Allende sample give ratios significantly different from cosmic. The sulfides from the wr-demineralized sample and the CAI-demineralized sample have very different Pt-metal ratios. Those of the wr-sulfide fraction approach the cosmic ratios; those of the CAI-sulfide fraction are highly fractionated, exhibiting very large excesses relative to cosmic in the Ru/Os and Ir/Os ratios due to the relatively low Os. This observation and the fact that the NiFe-silicate-oxide fractions for both samples are fractionated relative to cosmic and different from one another are additional factors to be considered in relation to matrix contamination of the CAI sample measured. The carbon-rich residues from both whole rock and CAI also do not have cosmic relative abundances of the Pt-metals.

Pt-metal ratios in carbon-rich residues were compared with literature data on Pt-metals in refractory metal particles found in CAIs [1]. The metal particles have fractionated Pt-metal ratios. Among these particles there are large variations of metal ratios which have been discussed by the various authors (e.g., Table 4 references). We expand our original table to include data on CAIs by Grossman and Ganapathy [16], recent results by Wark [9] on Os-rich metal nuggets which reproduce reasonably well the results of Blander et al. [8], data on Zelda fremdlinge OsRu nuggets by Armstrong et al. [10], and Zorba siderophiles by Grossman et al. 32], and the data on the separated phases and bulk rock samples reported here (Table 4).

Some Pt-metal ratios from the chemically separated fractions tend to correspond to those reported for refractory metal nuggets, Table 4. The wr NiFe-silicates-oxides and some of the metal nuggets of Wark and Lovering [5], the wr residue and the metal nuggets of Wark [9], and the CAI NiFe-silicates-oxides and Zelda OsRu nuggets with 10.04% Fe [10] have very similar Pt-metal ratios. The correspondence between the wr residue and metal nuggets might be anticipated if the residue scavenged the metal particles. There are no obvious reasons for the other correlations.

Discrete Pt-metal rich mineral phases in Allende do not, in general, have cosmic complements of these metals (e.g., Table 4). Element partitioning within and among various condensed phases in the solar nebula is expected to have occurred. What scale of aggregation or for what rock compositions do cosmic Pt-metal ratios become the rule? Bischoff and Palme [21] report experiments in which several discrete particles enriched in refractory metals in CAI A 37 were isolated. Bulk inclusion, Pt-metal rich bulk particles, fremdlinge contained in the particles and the individual complex metal, metal oxide and sulfide rich aggregates and mineral phases in the fremdlinge were analyzed. The masses of the material studied spans the amounts we measured and the microscopic results of others. The experiments included an 111 mg bulk CAI (A 37) and several 10–190 μg aliquots which contained single and composite microscopic phases. Results relevant to our work are the cosmic Os-Ru-Ir ratios in the bulk inclusion and the fractionated ratios in almost all the aliquots and their various included phases. An important result related to our observations is the identification of very small (1–2 μm) multiphase particles which have cosmic refractory metal relative abundances and show little evidence of low temperature alteration. The authors suggest that these are the carriers of the refractory metals in the bulk inclusion which were trapped within high temperature minerals of the inclusion at the time of their formation.

If the very small multiphase refractory metal particles are the primary contributors of refractory metals to the high temperature CAI oxides, they could have been released during the HF-HCl dissolution and if reactive remained in this solution or, if inert, were scavenged by the the insoluble residue. Since both of these separates give fractionated OsRuIr, the contribution from these multiphase particles must be small. Pt-metals in cosmic proportions in other submicroscopic phases appear to be required.

In conclusion, although the Pt-metals in "Allende space" were in cosmic proportions, material aggregated in various regions or under differing conditions acquired Pt-metals that were initially fractionated or became fractionated after aggregation. This has been noted before. Our results establish that there are a number of oxidized Pt-metal containing phases-metal nuggets correlations. A significant fraction of the Pt-metals are in submicroscopic phases in cosmic relative abundances. The different locations and conditions under which the various Pt-metal containing components of Allende evolved present a problem.

Part III. A Thermal History of Allende Components

The trace element data indicate that modeling the formation of an object like Allende is very complex. Not only were different reservoirs in the solar nebula sampled at different times but the thermal conditions varied greatly. We will discuss a final moderately high temperature (~800–1200 °C) thermal event experienced by components of Allende during which mineral alteration could have occurred.

The thermometry is based on the distribution of Hg between labile and retentive sites in silicates and oxides in response to temperature (e.g. [29]). Hg occupies at least two types of sites in silicates and oxides based on the results from stepwise and isothermal heating experiments. Most of the Hg volatilized at lower temperatures (130°, 250 °C) is released in a burst and, hence, must be associated with a phase or a site responsive to some type of threshold process. Release of the remainder of the Hg is by a diffusion mechanism. Detailed studies have been made on meteorites only, and in most cases all Hg released above 300° to 400 °C is released in this manner. Isothermal measurements at lower temperatures further confirm the diffusion mechanism by yielding $D/a^2(T)$ results that are collinear with higher temperature linear heating data on a log D/a^2 vs. $1/T$ plot [29]. It has been established that for silicates and oxides, in a closed system at

Table 5. Thermal data for Allende matrix and CAI samples.

Sample	wt (mg)	Mineralogy [a]	Crystallinity	[Hg] (ppb)	$\frac{Hg_{\leq 450^\circ}}{Hg_{>450^\circ}}$	T °C
"A"-mottlet [b]	177.5	mel, fas, sp, [b] gross, per	coarse	3.0	9.8	778
"B"-lavender [b]	35.1	mel, gross, sp, per, wo, hib	fine	4.7	4.7	870
Matrix around "B"	325.3			5.8	4.6	875
"C" single inclusion [b]	135.1	sp, neph, sod, cpx, per, mel	very fine	3.9	2.2	975
Chondrules	35	olivine?	–	37.5	4.6	875
CAI-bulk [c]	43.2	99% type-B	–	25	4.0	892
Whole rock-bulk [d]	145		–	2.6	0.23	1272

[a] Descriptions by Louis Fuchs (ANL).

[b] Inclusions described in [1]: mel = melilite, fas = fassaite, sp = spinel, gross = grossular, per = perovskite, wo = wollastonite, hib = hibonite, neph = nepheline, sod = sodalite, cpx = clinopyroxene.

[c] CAI-bulk excavated from several ares.

[d] Seven other 100–300 mg bulk Allende samples gave temperatures of ~670 °C; see text.

thermal equilibrium, the relative amounts of Hg in more retentive sites (i.e., >450 °C) increases with temperature.

Regionally metamorphic rock and igneous intrusive rocks were used to calibrate a temperature scale based on the ratio of Hg released up to and including 450 °C and that released above this temperature [29 and included references]. Post-crystallization exchange (retrograde effects) may not be a factor for Hg thermometry since exchange would be between low and high temperature sites. On cooling, Hg in high temperature sites would be expected to be frozen in and not transferred to low temperature sites. The Hg equilibration between retentive and labile sites at maximum regional metamorphic temperature is not reversed when the formation slowly cools to low temperatures. When an igneous intrusion cools, a closure temperature is reached. Further cooling does not cause reequilibration of Hg. In contrast to metamorphic systems, when temperatures are high enough to produce melts, very rapid quenching may give Hg equilibration temperatures of >800 °C corresponding to mineral closure temperatures.

The Hg thermometer has been applied to lunar low and high Ti basalts to yield 1125–1225 °C and 985 to 1140 °C, respectively; lunar volcanic glasses, 1095 °C and anorthositic tephra, 1185 °C. Hg equilibration temperatures for two lunar melt rocks of 1105 °C and 1090 °C can be compared with temperatures of 1080 °C and 998 °C, respectively, based on Ni-phosphide [33] and olivine-augite equilibration [34], respectively. The enstatite chondrites Hvittis and Abee have Hg equilibration temperatures of 930 °C and 750 °C, respectively; literature temperatures based on low pressure enstatite-diopside solvus [35] for E6 chondrites and metal carbide microstructure [36] for Abee are 870 to 910 °C and >700 °C, respectively.

Three different types of Allende inclusions were sampled and reported on briefly by Jovanovic and Reed [1]. Their detailed mineralogy was determined by L. Fuchs (ANL) on the basis of optical and x-ray examination. The inclusions are listed in Table 5 and their mineral compositions are given in the order of abundance. Hg thermal equilibration temperatures for these inclusions, for small ($\lesssim$1 mm) dark chondrules and for wr- and CAI-bulk samples from this work are listed in Table 5 along with the concentrations of Hg in each sample. For the "A", "B", and "C" inclusions, the equilibration temperatures 778, 870, and 975 °C, respectively, correlate with the crystallinity of the samples. This suggests crystal growth after aggregation to form the inclusion due to either slow cooling (Hg equilibration closure in the presence of Hg vapor) or to metamorphic/metasomatic reheating [19] or melting (e.g. [37]). The 778 °C equilibration temperature for coarse grained inclusion "A" is reasonable based on the presence of grossular which according to Clark et al. [30] (using experimental results of Yoder [38]) decomposes above 800 °C. Prograde metamorphism followed by slow cooling could have occurred. As noted, Hg equilibration is not responsive to retrograde metamorphism.

The presence of grossular in fine grained inclusion "B" can be explained by devitrification of a glass. The Hg distribution established at 870 °C did not reequilibrate at the grossular stability limit. However, a case for reheating can be made on the basis of the fact that the matrix in which inclusion "B" was imbedded (note that the quantity of matrix measured is ~10 times the amout of the inclusion) gives the same Hg equilibration temperature of 875 °C as the inclusion (870 °C). This material, which could not have been a melt, then, along with the inclusion experienced the same reheating event in an original, i.e., pre-Allende parental (accretional) object. This may have occurred after or simultaneously with the formation of furry coating of matrix crystals around CAI [25]. The composite CAI material measured in Part II gives an Hg equilibration temperature of 892 °C, which is close to that of inclusion "B", 870 °C and the chondrules discussed below.

The wr-bulk sample gives a very high Hg equilibration temperature (1272 °C) and has a low concentration of Hg. Although this could als be a Hg closure (quench) temperature for cooling in the nebula, it is possible that an open system heating event caused loss of Hg in low temperature sites. Typically, bulk (matrix) Allende Hg equilibration temperatures are ~670 °C [29].

The very fine grained inclusion "C" contains sodalite and nepheline which are associated with lower temperatures than the minerals in "A" and "B". Yet, "C" gives a higher (975 °C) Hg equilibration temperature. The presence of sodalite and nepheline suggests metasomatic alteration of primary minerals. Clark et al. [30] suggest solidification as a glass with subsequent devitrification for a fine grained nepheline-sodalite-fassaite-olivine chondrule. Rapid quenching from a melt followed by devitrification to give inclusion "C" is consistent not only with the very fine grain size but also with the Hg release pattern. In contrast to the other inclusions and matrix associated with "B" inclusion (Table 5), a large fraction (~30%) of the Hg in "C" was released in the >450–600 °C temperature step. This suggests that rapid cooling inhibited the redistribution of Hg from higher ($\geqq$600 °C) to lower ($\leqq$450 °C) temperature sites. Such a release pattern was observed in the 35 mg sample of dark condrules ($\lesssim$1 mm diameter) from Allende. A temperature of 875 °C was determined for these rapidly quenched droplets (Table 5). Inclusion "C" appears to have quenched and devitrified at a higher temperature than the chondrules. If Hg equilibration had continued in the "C" inclusion so that the >450–600 °C fraction was transferred to $\leqq$450 °C sites, a temperature of 900 °C is estimated, which is close to the equilibration temperature of the other inclusions.

The Hg equilibration temperatures refer to final significant thermal events experienced by Allende material. Some of these occurred prior to the formation of the Allende parent body. These temperatures are all lower than the >1160 °C for the initial nebular condensation and aggregation of components of Allende (e.g., Clayton et al. [39], Stopler [40]).

The temperatures listed in Table 5 are in the range of those (800–900 °C) required by Armstrong et al. [10] for the sulfidization of precursor metal in the Zelda inclusion. These authors also note that CAIs existed for "reasonable" periods of time at ~850 °C based on phase relationships. We propose that the chondrules Hg equilibration temperature of 875 °C is a closure temperature on cooling from a liquid to a glass followed by devitrification. However, Haggerty and McMahon [28] postulate a <1000 °C temperature for reequilibration to account for the evolution of magnetite-sulfide metal complexes in olivine-rich condrules in Allende. This would also apply to CAIs (see [18]) if present in the same assemblage as the chondrules. Blum et al. [18] determined that oxidation of nebular metal could have occurred between 600 and 900 °C depending on the oxygen fugacity. They also calculate that εRu-Fe exsolves from NiFe in CAIs isothermally at 500 °C (preferred temperature) or during very slow cooling through this temperature range. The Hg equilibration would not respond to these lower temperatures unless new Hg became available when the system experienced these temperatures. This could be the case for most of the bulk (matrix) samples where the concentrations of Hg are much higher (×10) than those in the CAIs, and the equilibration temperature is, as noted, ~670 °C.

Conclusions

1. Large fractions of refractory noble metals are present in sulfildes in both Allende whole rock and in coarse grained inclusions. The appreciable amount (~1%) of sulfide in the CAI samples measured is not matrix contamination related to laboratory isolation of CAI material. The CAI-bulk and the summation-of-demineralization fractions have near-cosmic and noble metal rations, respectively. This was also observed by Grossman and Ganapathy [16]. The ratios in the whole rock sulfide fraction also approache cosmic. All other demineralization fractions and the summed whole rock sample have highly fractionated noble metal ratios relative to cosmic as is the case for all the metal particles reported in the literature. There

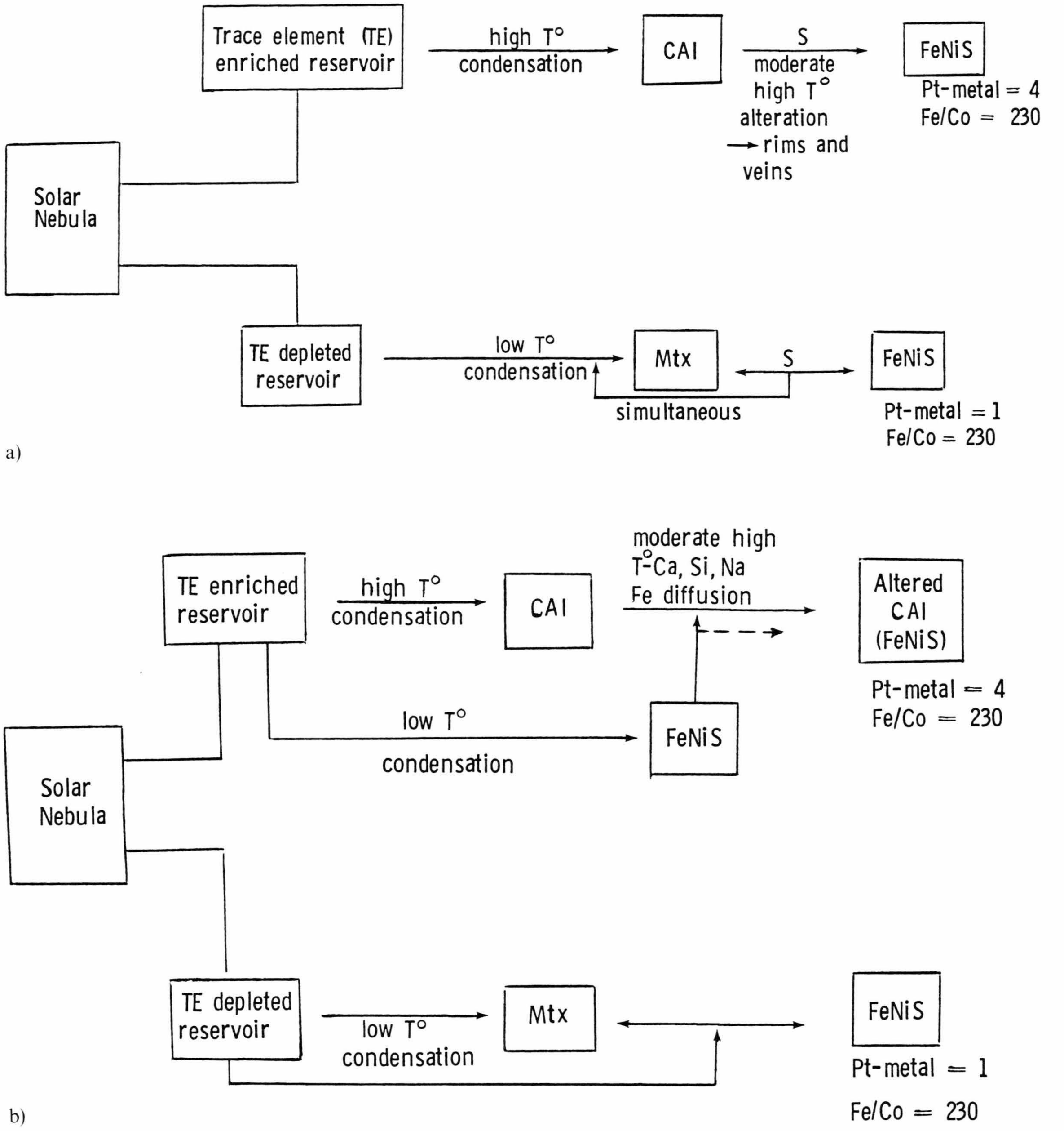

Fig. 1. Solar nebula processes that could account for the Pt-metal concentrations and Fe/Co ratios in Allende whole rock (matrix) and CAI sulfides. a) The high temperature condensates and low temperature condensates in the Allende region of the solar nebula aggregated into CAI material and matrix material with relative Pt-metal contents of 4 : 1, respectively. b) FeNiS formed in the trace element depleted and enriched reservoirs at lower temperature after the high temperature CAI constituents condensation.

is a correspondence between some of these fractionated Pt-metal ratios and those reported for metal particles. This may have implications for the evolution of materials in the solar nebula.

2. The Fe/Co ratios, for the whole rock and the CAI sulfides are the same (~230). The CAI-bulk and carbon-rich residue also have this ratio as do the sulfides in the Zelda fremdlinge.

3. CAIs of various lithologies have been subjected to thermal equilibration at 780–975 °C probably after accretion of condensates to form inclusions and before incorporation into Allende or pre-Allende parental object, where lower temperature (~670 °C) reequilibration could have occurred. Although most bulk matrix samples equilibrated Hg at ~670 °C, the wr-bulk sample measured in Part II gives a 1272 °C temperature, which could be nebular or be due to an outgassing event.

To account for the differences in the concentrations of Pt-metals in the coarse grained inclusions vs. bulk Allende meteorite (matrix predominantly) it seems necessary to conclude that the components of each formed in solar nebula regions where, or at times when, Pt-metal concentrations and temperatures were different. From concentration and thermal history points of view, two distinct reservoirs are needed.

To account for the large fractions of the Pt-metals in oxidized states, it is necessary to postulate that oxidation (sulfidization) occurred when Pt-metals in pristine condensates reacted with fluids (gases) that were sulfide enriched. The presence of sulfides that are chemically identical in the Fe/Co ratios in the matrix and inclusions, constrains the manner in which each acquired and remobilized (i.e., metamorphized/metasomatized) Pt-metal phases. Possible models for the processes that occurred are outlined in Figures 1 a, b. The models apply only to "Allende-space", other meteorites would have their own environments (see, for instance, [14]).

In Fig. 1 a, the high temperature condensates and low temperature condensates in the Allende region of the solar nebula aggregated into CAI material and matrix material with relative Pt-metal contents of 4 : 1, respectively. Both experienced sulfidization at moderate temperatures (800° – 1000 °C) with matrix continuing to thermally, but not chemically, equilibrate to lower temperatures (~600 °C) before the final parent body to Allende formed. The Fe/Co ratio of 230 for the sulfide phases in the whole rock and CAI material may reflect a limit on the extent of the sulfidization reaction.

In Fig. 1 b, FeNiS was formed in the trace element depleted and enriched reservoirs at lower temperature after the high temperature CAI constituents condensation. This sulfide became associated with the high temperature condensate at the time of its metasomatism/metamorphism. In this case the sulfidization reaction occurred independently of the CAI thermal alteration.

Acknowledgements

Work supported by NASA. The manuscript was significantly improved by constructive reviews and comments by F. Wlotzka, H. Palme and an unidentified reviewer.

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Nachdruck — auch auszugsweise — nur mit schriftlicher Genehmigung des Verlages gestattet
Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg