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Low-temperature exsolution in refractory siderophile element-rich opaque assemblages from the Leoville carbonaceous chondrite

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ABSTRACT

A model for the formation of opaque assemblages in refractory inclusions in C3V chondrites was proposed by Blum et al. [1,2], in which the assemblages formed not by direct condensation but by crystallization from siderophile element-rich droplets within molten silicate inclusions, followed by low-temperature exsolution and oxidation and/or sulfidation. Although the data presented do not address the high-temperature histories of these objects, we describe herein two opaque assemblages in a Leoville refractory inclusion which provide the strongest textural and chemical evidence yet found in natural samples for the relatively low-temperature equilibration called for in this model. The assemblages have fine ($< 1 \mu\text{m}$ across) lamellae of $\epsilon\text{Ru-Fe}$ in $\gamma\text{Ni-Fe}$, with sharp contacts between phases. The larger ($35 \times 35 \mu\text{m}$) of the two assemblages, OA1, has sets of regularly spaced, parallel lamellae, demonstrating crystallographic control. In the other, OA2, Ir and Pt partitioning between lamellae and host is consistent with equilibration at $\sim 873 \text{ K}$, as are the Fe, Ni and Ru contents of coexisting $\epsilon\text{Ru-Fe}$ and $\gamma\text{Ni-Fe}$ and the narrow widths of the lamellae in both assemblages. The bulk compositions of the two assemblages bracket a previously inferred phase boundary in the Fe-Ni-Ru system at 873 K . In these assemblages, the observed phases and their compositions are as predicted by the inferred phase relations at this temperature, suggesting that the position of the inferred phase boundary is correct. This is the same equilibration temperature estimated by Blum et al. [2] for another opaque assemblage from Leoville, also on the basis of alloy compositions and inferred phase equilibria in the Fe-Ni-Ru system. The similarity of results for different Leoville samples is consistent with the suggestion [2] that final equilibration of the assemblages was post-accretionary.

1. Introduction

Calcium-, aluminum-rich inclusions (CAI's) in carbonaceous chondrites are of great interest and importance because they are composed of many of the high-temperature minerals (e.g., hibonite, spinel, melilite and fassaite) predicted to have formed as refractory condensates early in the cooling history of the solar nebula [3]. The inclusions are enriched in refractory trace elements by a factor of ~ 20 relative to C1 chondrites [4]. Refractory lithophile trace elements are contained in silicates, hibonite and perovskite, whereas refractory siderophiles (W, Os, Re, Ir, Pt, Mo, Ru, Rh) are concentrated into micrometer-sized pure metal or alloy nuggets or into multi-phase aggregates, which vary in shape from irregular to round. The largest one yet found is

$\sim 1000 \mu\text{m}$ across [5], but most are between 1 and $50 \mu\text{m}$ across [6]. The aggregates typically consist of Ni-Fe metal enclosing micrometer sized nuggets of refractory siderophile metals or alloys (e.g., Re-Os, Ir-Pt and Ru-Os). Oxides (most commonly magnetite), sulfides such as pyrrhotite (Fe_{1-x}S), molybdenite (MoS_2) and pentlandite [$(\text{Fe}, \text{Ni})_9\text{S}_8$] and Ca-phosphates such as apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$] or whitlockite [$\text{Ca}_3(\text{PO}_4)_2$] may also be present, and rims of V-rich magnetite and/or V-rich fassaite around the assemblages are common. Because the refractory siderophiles are predicted to be among the first elements to condense from a cooling gas of solar composition [3], and because these assemblages are found enclosed in all major CAI phases, many workers concluded that they are direct condensates that formed before CAI's, either pre-

solar materials [6] or condensates from the solar nebula that formed under relatively oxidizing [7,8] and possibly sulfidizing [5] conditions, and that were later incorporated into CAI's as solids, perhaps followed by additional sulfidation [5]. Because of their presumed pre-CAI history, the assemblages were termed "*Fremdlinge*", German for "foreigners", by El Goresy et al. [9]. We use the non-genetic term "opaque assemblage", rather than "*Fremdling*", in this paper.

Blum et al. [2], noting that the sharp composition contrasts observed between coexisting alloys in opaque assemblages should not have survived CAI melting and interpreting the alloy compositions in terms of phase equilibria in the Fe-Ni-Ru system [10], proposed a model in which the opaque assemblages do not predate CAI's and are not pristine high-temperature condensates. According to this model, droplets of immiscible alloy melts formed within molten CAI's. All the siderophile elements strongly partitioned into these droplets, which crystallized as homogeneous alloys before undergoing low-temperature exsolution into Ni-Fe and refractory siderophile element-rich alloys during oxidation and/or sulfidation.

Unfortunately, oxidation and sulfidation tend to destroy primary textures by creating new minerals, as is typically the case in Allende opaque assemblages. As a result, although the arguments for exsolution [2,10] are theoretically sound, there has been little unambiguous textural and chemical evidence of exsolution in natural samples to support them. Blum et al. [2] studied an assemblage from Leoville, LEO 575-OA1, which contains what they interpreted as two lamellae of γ Ni-Fe and two lamellae of ϵ Ru-Fe which exsolved from their α Fe host. (In Blum et al. [2,10] and in this paper, the α , γ , and ϵ designations are based on phase compositions and not on determinations of crystal structures.) Because there are only two grains of each alloy and they are not oriented parallel to each other (e.g., the ϵ Ru-Fe laths intersect), the textural evidence that these crystals are exsolution lamellae is not conclusive. Other workers [7,11] reported observations of very fine ($\sim 0.25 \mu\text{m}$ across) lamellae of Os-Ru alloys in Ni-Fe. Quantitative analyses of these needles were not, understandably, presented in these papers, however, so Fe-Ni-Ru

phase equilibria could not be used to evaluate an exsolution origin for the Ru-rich alloys in those assemblages. Whereas these studies may provide textural evidence but no chemical arguments for the exsolution origin of Ru-rich alloys, Blum et al. [2], on the other hand, presented strong chemical evidence but unconvincing textural evidence for exsolution. We report here the discovery of opaque assemblages with both clear textural and chemical evidence of a major role for exsolution and equilibration at relatively low temperatures in the formation of refractory siderophile element-rich assemblages, and we use the observed phase compositions to bracket a previously inferred phase boundary in the Fe-Ni-Ru system. We also report the first meteoritic occurrence of goldmanite (vanadian garnet).

2. Analytical methods

The assemblages were examined with a JEOL JSM-35 scanning electron microscope equipped with a Kevex 7077 energy dispersive X-ray system (EDS), which was used for phase identification and preliminary analysis. Alloy compositions were determined with a fully automated Cameca SX-50 electron microprobe, equipped with four wavelength dispersive spectrometers and a Kevex EDS. Pure metal standards were used for all elements except S (FeS) and P (synthetic $\text{Ca}_2\text{P}_2\text{O}_7$). Analyses were performed at 15 kV with a beam current of 50 nA. For alloys of these compositions, the vast majority of the secondary X-rays are generated within a spherical volume which is slightly less than $1 \mu\text{m}$ in diameter under these conditions [12]. Data were reduced via the modified ZAF correction procedure PAP [13]. Additional correction factors were determined by analysis of pure metals for the following peak overlaps: Re M_α -W M_β , Os M_α -Re M_β , Ir M_α -Os M_β , Pt M_α -Ir M_β , Rh L_α -Ru L_β , and S K_α -Mo L_α . Before correction, analytical sums ranged from 99 to 109 wt%; after correction for overlaps, totals ranged from 95 to 101 wt% and were normalized to 100 atom%.

3. Sample description

We analyzed in detail two opaque assemblages in L1, a compact Type A inclusion found in the

Leoville C3V chondrite and described by Simon and Grossman [14]. Both assemblages occur in melilite. OA1, shown in Fig. 1a, is approximately

$35 \times 35 \mu\text{m}$. It consists predominantly of $\gamma\text{Ni-Fe}$, with a core of αFe , lamellae of $\epsilon\text{Ru-Fe}$ up to $1.5 \mu\text{m}$ in width, and oriented submicrometer sulfide

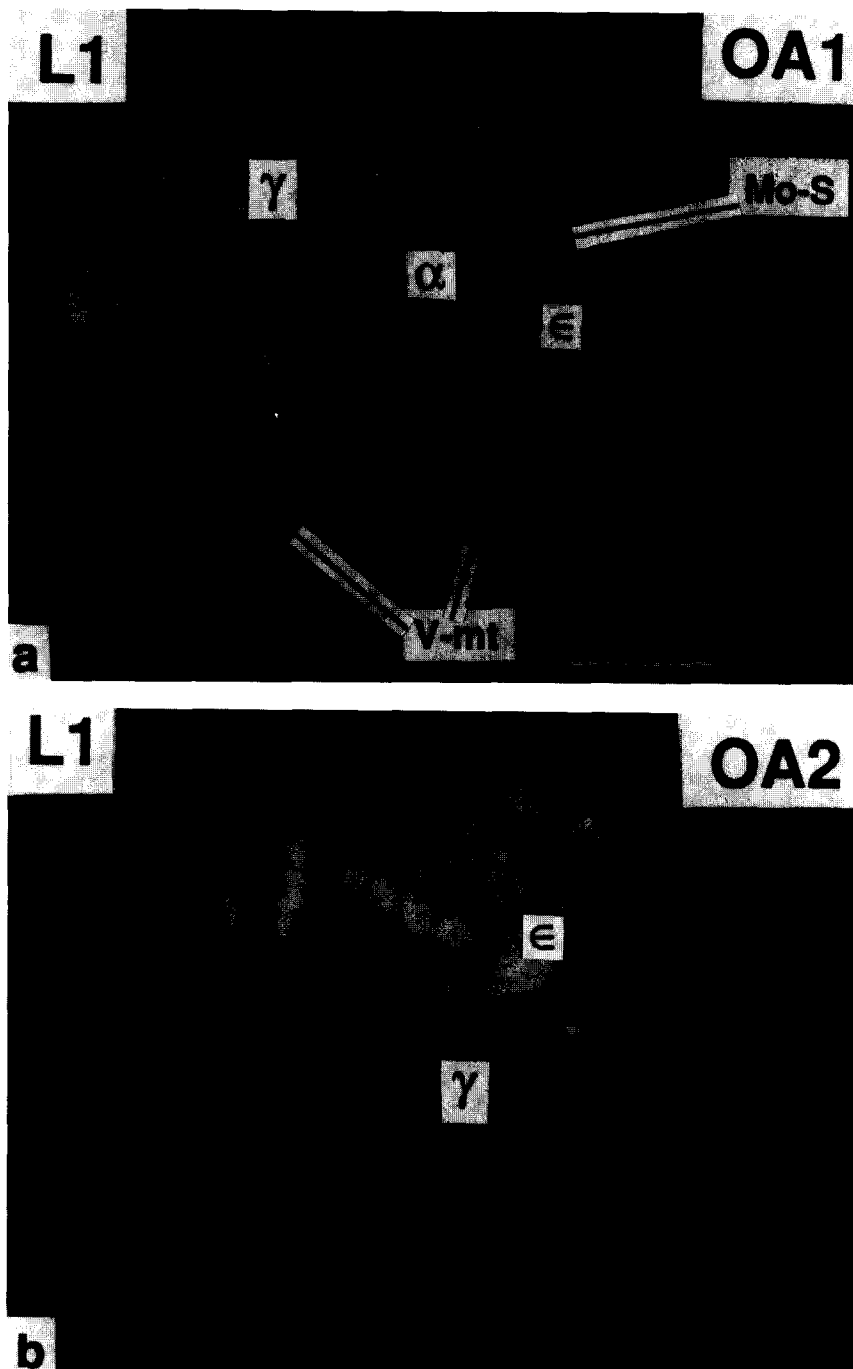


Fig. 1. Backscattered electron images of opaque assemblages in CAI L1. $\gamma = \gamma\text{Ni-Fe}$; $\alpha = \alpha\text{Fe}$; $\epsilon = \epsilon\text{Ru-Fe}$; $V\text{-mt} = \text{V-rich magnetite}$; $Mo\text{-S} = \text{Mo-sulfide}$. (a) AO1. Note sets of parallel lamellae of $\epsilon\text{Ru-Fe}$, and, especially in the lower left, oriented sulfide needles (black). Scale bar is $10 \mu\text{m}$. (b) OA2. Only $\gamma\text{Ni-Fe}$ and $\epsilon\text{Ru-Fe}$ are present. Scale bar is $1 \mu\text{m}$.

grains which EDS and wavelength-dispersive spectra indicate are Mo-sulfide. Note that, unlike the assemblages studied by Blum et al. [2], this assemblage has sets of parallel, equally spaced ϵ Ru-Fe lamellae with fairly uniform thicknesses, indicating exsolution along crystallographically controlled planes in the host γ Ni-Fe. In contrast, V-rich magnetite occurs in discontinuous, ribbon-like patches near the rim. There are also several small (2-3 μ m) grains of V-rich fassaite (not visible in Fig. 1a) adjacent to OA1.

OA2 (Fig. 1b) is smaller (~ 10 μ m across) than OA1 and is also dominated by γ Ni-Fe. It has lamellae of ϵ Ru-Fe up to 1 μ m in width, but does not contain α Fe. An interesting feature of this opaque assemblage is that it is not associated with V-rich magnetite or fassaite, but instead, as shown in Fig. 2, it is partially enclosed by goldmanite, a vanadian garnet. The composition of this goldmanite is given in Table 1, along with that of the type material [15]. The compositions are quite similar, neither is end-member $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$. Both contain Al, Fe^{3+} and Ti, and little or no Mg and Mn. The formula of the meteoritic goldmanite is approximately $\text{Ca}_3(\text{V}_{1.22}\text{Al}_{0.46}\text{Fe}_{0.18}\text{Ti}_{0.13})(\text{Si}_{2.87}\text{Al}_{0.13})\text{O}_{12}$, assuming that

the Fe is trivalent and that it does not enter the tetrahedral site. Substitution of trivalent ions for tetrahedral silicon is necessitated by the substitution of tetravalent Ti for trivalent ions in the octahedral site. Tetrahedral Fe^{3+} is also possible. Both Fe^{3+} and Al^{3+} are known to enter the tetrahedral site in garnet but it is not clear if either ion is preferentially taken into the tetrahedral site relative to the octahedral site [16]. Moench and Meyrowitz [15] suggested that the name goldmanite applies to all Ca-garnets in which V is more abundant than all the other octahedrally coordinated cations combined. This being the case for the material described herein, this is the first reported occurrence of goldmanite in a meteorite.

4. Results

Representative wavelength-dispersive electron probe analyses of the alloys in the two opaque assemblages are given in Table 2. Because the dimensions of the analytical volumes approach the dimensions of the ϵ Ru-Fe lamellae which were analyzed, we cannot rule out the possibility that the analyses of ϵ Ru-Fe are very slightly

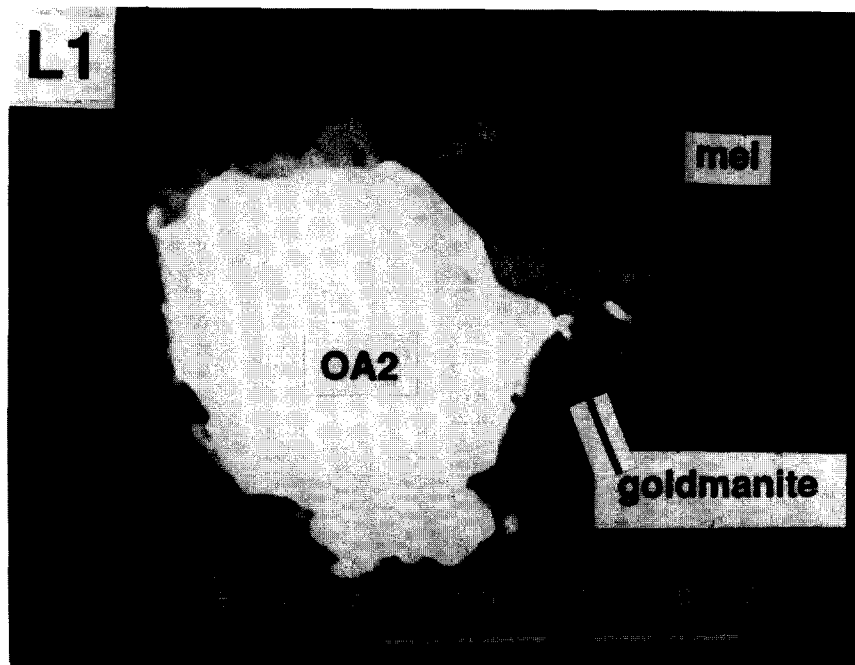


Fig. 2. Backscattered electron image of OA2 showing the adjacent goldmanite (*mel* = melilite). Scale bar is 10 μ m.

TABLE 1

Goldmanite compositions

	OA2		Type material ²
	Average ¹	Range	
SiO ₂	35.3	33.7–36.0	36.6
Al ₂ O ₃	6.2	4.8– 8.3	4.9
TiO ₂	2.1	0 – 7.1	0.25
V ₂ O ₃	18.7	16.6–21.0	18.3
Fe ₂ O ₃	3.0	0.6– 6.8	5.4
MgO	0.1	0 – 0.4	0.7
MnO	–	–	0.3
CaO	34.6	33.8–35.4	33.3
<i>Cations per 12 oxygen ions</i>			
Si	2.87		2.98
^{IV} Al ^a	0.13		0.02
Total tet. site	3.00		3.00
^{VI} Al	0.46		0.45
Ti	0.13		0.02
V	1.22		1.20
Fe ³⁺	0.18		0.33
Total oct. (Y) site	1.99		2.00
Mg	0.01		0.08
Mn	–		0.02
Ca	3.01		2.91
Total X site	3.02		3.01
Total cations	8.01		8.01

¹ Average of seven energy-dispersive analyses, normalized to 100 wt%. Total iron calculated as Fe₂O₃.

² Wet chemical analysis [15]. Total iron calculated as Fe₂O₃.

^a Upper limit for tetrahedral Al. Fe³⁺ may also enter the site, in addition to or instead of Al.

contaminated by adjacent phases. Unlike the energy-dispersive analyses of Blum et al. [2], our analyses show measurable amounts of W and Rh in the alloys. Mo and S appeared in most analyses of γ Ni-Fe and ϵ Ru-Fe in OA1, including those in Table 2. Mo always occurred with S, several analyses have atomic Mo:S ratios of 1:2, and analyses with no S have no Mo (but do contain W). Many discrete sulfide grains are present, and EDS and wavelength-dispersive spectra indicate that they contain large amounts of Mo. We therefore attributed the minor (up to 2.5 atom%) Mo abundances to unavoidable, submicrometer grains of Mo-sulfide, which we assumed to be molybdenite (MoS₂), subtracted Mo and S from the analyses in 1:2 atomic proportions, and renormalized the analyses on a Mo-free basis. About half

(11/20) of the analyses had S left over (i.e., in excess of the amount needed to convert the Mo in the analysis to MoS₂). These residuals range from 0.14 to 0.71 atom%, and they may represent S present in the alloys. Alternatively, they may be due to submicrometer Fe-sulfide grains.

The results show that the γ Ni-Fe and ϵ Ru-Fe in OA2 are richer in Ru and poorer in Fe than their counterparts in OA1 and that α Fe is poorer in Os, Ir and Ru and richer in Fe than both γ Ni-Fe and ϵ Ru-Fe. These characteristics and the lack of α Fe in OA2 indicate that there is a difference in bulk composition between the two assemblages—namely, a higher Fe/Ru ratio in OA1 than in OA2. Caillet et al. [11], in a study of an opaque assemblage in a Vigarano CAI, also observed higher Os (2–3 vs. 1.5–1.74 wt%), Ir (1.5–2.13 vs. 1.4–1.64%) and Ru (0.52–0.67 vs. 0.18–0.29%) contents in γ Ni-Fe relative to coexisting α Fe, but, in our sample, the compositional differences between the two phases are greater (e.g., 5.67 vs. 0.99 wt% for Os, 8.40 vs. 3.95% for Ir, and 7.72 vs. 2.18% for Ru, in representative analyses of γ Ni-Fe and α Fe, respectively). In both OA1 and OA2, the ϵ Ru-Fe is enriched in Os, Re and W and depleted in Ni, Pt and Rh

TABLE 2

Representative analyses of phases in OA1 and OA2 (atom%)

	OA1			OA2	
	γ Ni-Fe	ϵ Ru-Fe	α Fe	γ Ni-Fe	ϵ Ru-Fe
S	–	0.29	0.05	–	–
V	0.22	0.13	–	0.09	0.08
Fe	70.23	67.00	88.85	69.95	63.65
Co	0.22	0.18	0.76	0.20	0.25
Ni	11.60	6.24	3.33	13.38	4.23
Si	0.19	0.14	0.09	0.16	0.41
W	0.15	0.48	0.08	0.04	1.59
Re	0.15	0.54	0.05	0.15	0.66
Os	2.30	6.51	0.34	2.28	7.94
Ir	3.38	3.22	1.33	2.31	3.71
Pt	4.76	1.13	3.03	3.82	0.77
Ru	5.92	13.59	1.40	6.70	16.23
Rh	0.87	0.56	0.69	0.92	0.48

P, Cr and Ti were sought but not detected. Mo was detected in some analyses but was attributed to MoS₂ and subtracted from the analyses along with the appropriate amount of S.

Average 2 σ relative uncertainties based on counting statistics are: $\pm 0.6\%$ for Fe, $\pm 1\%$ for Ru, $\pm 2\%$ for Ni, Os, Ir and Pt, $\pm 3\%$ for S and W, $\pm 4\%$ for Rh, $\pm 10\%$ for Re, $\pm 12\%$ for Si, $\pm 30\%$ for Co ($\pm 8\%$ in α Fe), and $\pm 40\%$ for V.

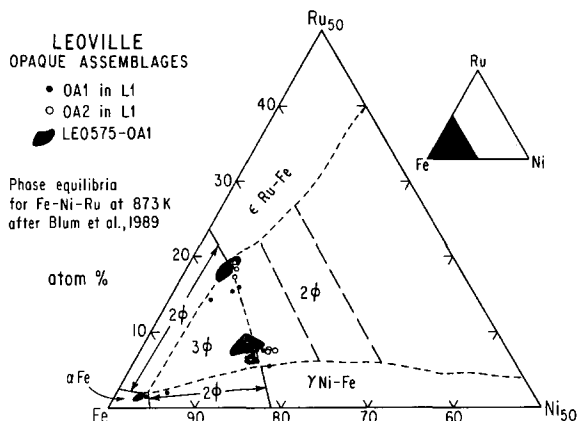


Fig. 3. Compositions in atom% of alloys in OA1 and OA2 compared to those in another opaque assemblage from Leoville, LEO575-OA1 [2], and to phase equilibria in the Fe-Ni-Ru system [10]. The analyses are consistent with equilibration of the assemblages at ~ 873 K. Solid lines indicate phase boundaries extrapolated a short distance from experimentally determined ones in binary systems; short dashes indicate phase boundaries inferred by Blum et al. [10]; long dashes are schematic tie-lines.

relative to the coexisting γ Ni-Fe. In OA1, α Fe is the phase richest in Co and poorest in Ni. The most abundant of the noble metals in α Fe is Pt.

To simplify comparison with the Leoville assemblage (LEO 575-OA1) analyzed by Blum et al. [2], our data are plotted with theirs in terms of atom% Fe, Ni and Ru in Fig. 3, which also shows phase equilibria in the system [10]. Some of our analyses overlap with and others plot very close to those of Blum et al. [2]. In all three of these Leoville assemblages, the alloys have fairly uniform compositions and contacts between the phases are sharp.

5. Discussion

The model for the origin of refractory element-rich opaque assemblages, as summarized by Armstrong et al. [5], calls for condensation of the refractory siderophile elements into metallic nuggets, condensation of Ni-Fe metal, partial oxidation of the Ni-Fe to magnetite (possibly accompanied by sulfidation), and cold agglomeration and partial sintering of the above phases possibly accompanied by sulfidation, followed by incorporation of these solid assemblages into molten CAI's and possibly additional sulfidation. In the Armstrong et al. [5] model, the assemblages were

incorporated into CAI's prior to crystallization of spinel from CAI melts, which begins at temperatures of > 1800 K [17]. Because metal-magnetite assemblages are not stable at temperatures of $> \sim 770$ - 970 K [18], however, high CAI cooling rates were invoked by Armstrong et al. [5] to allow preservation of opaque assemblages. These workers found that the necessary rates were unrealistically high, based on experimental work and textures of CAI's [17], and admitted their inability to explain the survival of opaque assemblages in CAI's in the context of their model.

Palme and Wlotzka [19] and Armstrong et al. [5] noted that refractory metal nuggets in opaque assemblages may have formed via exsolution from Ni-Fe at relatively low temperatures. Blum et al. [20] and Bischoff [21] proved experimentally that this was possible. Blum et al. [1,10] pursued this line of investigation by conducting experiments on relatively Fe-poor compositions in the Fe-Ni-Ru system at 1273, 1073 and 873 K. From these results and previously published work (including the binary joins in the system), they constructed phase diagrams for these temperatures, inferring the equilibria for Fe-rich compositions. They also inferred the relationships in the system at 773 K. Blum et al. [2] used the diagrams to derive equilibration temperatures of ~ 873 K for an opaque assemblage from a Leoville CAI, and temperatures of ~ 770 K were found for some Allende assemblages. Blum et al. [10] also determined the diffusion coefficient for Ru in Ni and, from this result, Blum et al. [2] concluded that the observed sharp composition contrast between ϵ Ru-Fe and γ Ni-Fe could not have survived CAI melting. According to Blum et al. [2], diffusion should have created detectable Ru concentration gradients in ~ 30 s at 1473 K and nearly complete homogenization of the two alloys during cooling of the CAI, even assuming the minimum reasonable starting temperature (1550 K) and the maximum reasonable cooling rate of 200 K hr^{-1} [17]. Similarly, Armstrong et al. [18] noted that Pt-rich metal nuggets should readily dissolve in Ni-Fe upon heating, and they therefore concluded that the Pt nuggets formed by exsolution from Ni-Fe during sulfidation, late in the history of the opaque assemblage. They did not invoke such an origin for other phases in the assemblages, favoring instead origin by cold accretion of grains

previously formed under a wide variety of T - f_{O_2} conditions. In the Blum et al. [1,2] model, on the other hand, none of the minerals in opaque assemblages are pristine condensates that somehow retained their identities and chemical compositions through CAI melting, although, more recently, a rather convincing case has been made [22] that some mineralogical and chemical characteristics of an unusual, magnesiowüstite-bearing *Fremdling* survived the melting of its host CAI. In the Blum et al. [1,2] model, the minerals in opaque assemblages formed instead from droplets of immiscible alloy melts within molten CAI's. The siderophile elements strongly partitioned into these droplets, which crystallized as homogeneous alloys before undergoing low-temperature exsolution and loss of Fe during oxidation and/or sulfidation.

In addition to Fe, opaque assemblages also lost V by oxidation and diffusion into the surrounding silicates and spinel. This would be expected if the host CAI's cooled along the solar gas T - f_{O_2} curve [2]. This typically resulted in V-enrichment of nearby spinel [5,18] or, as in OA1, the formation of V-rich magnetite and/or V-rich fassaite adjacent to the assemblages. As is the case for OA1, there is no spinel in the immediate vicinity of OA2 to take up the oxidized V. When V_2O_3 entered the silicate adjacent to OA2, goldmanite formed instead of magnetite or fassaite, perhaps reflecting an unusually high V content in OA2 and/or unusual P - T - f_{O_2} conditions in the immediate vicinity of OA2. As many opaque assemblages enclosed in melilite have V-fassaite mantles [5], formation of goldmanite instead of fassaite around OA2 cannot be ascribed to the fact that OA2 has a melilite host. It is also unlikely that an unusual CAI bulk composition was responsible for formation of goldmanite instead of V-rich fassaite around OA2, as V-rich fassaite, and not goldmanite, is found adjacent to OA1 in the same CAI. Unfortunately, not enough is known about the P - T stability fields of goldmanite and V-fassaite or the origin of compact Type A inclusions to speculate further on why goldmanite, rather than V-fassaite, formed adjacent to OA2.

Our assemblages, especially OA1, provide the best textural evidence for low-temperature exsolution yet found in natural samples. Blum et al.

[10] found that annealing a homogeneous Ni-Fe-Ru alloy at 873 K produced a sample with very thin ($< 1 \mu\text{m}$), parallel lamellae, whereas annealing at higher temperatures (e.g., 1073 K) resulted in blebby exsolution of $\epsilon\text{Ru-Fe}$ grains 1 – $5 \mu\text{m}$ across. Bischoff [21] annealed an alloy with the bulk composition of an opaque assemblage from an Allende CAI for one week at 1173 K and also observed blebby exsolution (of Os-rich grains) in the run product. The differences in thickness of the lamellae are probably due to differences in diffusion rates, with slower rates at lower temperatures resulting in thinner lamellae [10]. The fact that the lamellae in OA1 and OA2 are $< 1 \mu\text{m}$ in thickness suggests that they formed at a temperature of $< 1073 \text{ K}$.

Phase compositions in OA1 and OA2 are also consistent with equilibration at $\sim 873 \text{ K}$ based on Fe-Ni-Ru phase equilibria. In the phase diagram for 873 K constructed by Blum et al. [10], the compositions of the three phases in the Leoville CAI analyzed by Blum et al. [2] and the three phases in OA1 plot near the apices of the triangular, three-phase ($\alpha\text{Fe-}\epsilon\text{Ru-Fe-}\gamma\text{Ni-Fe}$) field inferred by Blum et al. [10], as shown in Fig. 3. The difference in composition between the two alloys in OA2 is also consistent with the size of the miscibility gap inferred by Blum et al. [10] to exist for the two-phase (ϵ - γ) field at 873 K (Fig. 3).

The bulk composition of assemblage OA1 plots to the left of the boundary between the three-phase field and the two-phase field inferred by Blum et al. [10], and that of OA2 plots to the right. The fact that OA1 consists of the three phases αFe , $\gamma\text{Ni-Fe}$ and $\epsilon\text{Ru-Fe}$ and OA2 of the two phases $\gamma\text{Ni-Fe}$ and $\epsilon\text{Ru-Fe}$ provides the first confirmation of the location of the field boundary from either natural or artificial alloys.

Our data are also consistent with results of experiments on the partitioning of Pt and Ir between coexisting $\epsilon\text{Ru-Fe}$ and $\gamma\text{Ni-Fe}$ at 873 K [10]. In OA2, which contains only these two phases, the average $\text{Pt}_{\epsilon\text{Ru-Fe}}/\text{Pt}_{\gamma\text{Ni-Fe}}$ ratio is 0.20 ± 0.04 , within error of the value of 0.16 determined experimentally at 873 K by Blum et al. [10]. The average $\text{Ir}_{\epsilon\text{Ru-Fe}}/\text{Ir}_{\gamma\text{Ni-Fe}}$ in OA2 is 1.46 ± 0.12 , also very close to the experimental value (1.6) at 873 K.

Thus, the textures and Fe-Ni-Ru systematics in OA1 and OA2, and the Pt and Ir partitioning in

OA2, are all consistent with equilibration of these assemblages at ~ 873 K.

Low equilibration temperatures (~ 770 K) have also been proposed for opaque assemblages from Allende [2] and Vigarano [23]. In the latter work, Caillet et al. based their estimate on the compositions of coexisting kamacite and taenite in a large metal grain. This grain also contains Os-Ru needles, which, Caillet et al. [23] concluded, formed *in situ* at ~ 770 K.

It is likely that the fine exsolution textures observed in opaque assemblages from Leoville and Vigarano survived because, unlike those in Allende, the assemblages are relatively unaffected by late alteration. OA1 and OA2, for example, have not undergone the pervasive oxidation (except for V) or sulfidation that probably would have erased their original textures by changing their mineralogy and phase compositions, as in Allende. For example, formation of magnetite (which contains very little Ni) by oxidation of γ Ni-Fe tends to enrich the residual metal in Ni and deplete it in Fe. Sulfides may contain Ni and some Ru [17] but they exclude the other refractory siderophiles, except Mo. Formation of large proportions of sulfide, such as are found in many Allende opaque assemblages, also removes Fe from the metallic alloy and leads to oversaturation of the residual metal in refractory siderophiles, causing formation of relatively large refractory metal nuggets. In addition to Fe-Ni-Ru phase equilibria, Blum et al. [2] were able to apply Fe-Ni-S equilibria to the interpretation of phase compositions in a group of Allende opaque assemblages from CAI's, chondrules and the matrix. They determined equilibration temperatures of ~ 770 K, with f_{S_2} and f_{O_2} greater than those of a solar gas. Because the assemblages from different components of the meteorite indicate similar equilibration conditions, Blum et al. [2] suggested that final equilibration occurred after the components had been brought together, possibly on the Allende parent body. Our Leoville samples indicate an equilibration temperature (873 K) which is similar to that determined for the Leoville assemblage analyzed by Blum et al. [2] and which is also consistent with post-accretionary equilibration, in this case on the Leoville parent body. At least one other CAI, 3537-1, is known to have last cooled through this tempera-

ture while in the Leoville parent body. Caillet et al. [24,25] presented petrographic and isotopic evidence that this inclusion accreted in a hot and partially molten state into Leoville long after its original solidification.

6. Conclusions

(1) The opaque assemblage OA1 provides clear textural evidence for exsolution of ϵ Ru-Fe from γ Ni-Fe. In both OA1 and OA2, the presence of thin ($< 1\mu\text{m}$) lamellae, rather than coarser ($1\text{--}5\mu\text{m}$) blebs, is consistent with equilibration at < 1073 K, based on the experiments of Blum et al. [10].

(2) From phase equilibria in the Fe-Ni-Ru system, the compositions of the three alloys in OA1 and the two in OA2 indicate equilibration at ~ 873 K, the same temperature as that determined for another Leoville opaque assemblage [2].

(3) The partitioning of Pt and Ir between ϵ Ru-Fe and γ Ni-Fe in OA2 is similar to that observed in samples annealed at 873 K [10], also indicating equilibration of OA2 at that temperature.

(4) Bulk compositions of OA1 and OA2 bracket a previously inferred boundary between three-phase (α - ϵ - γ) and two-phase (ϵ - γ) fields in the Fe-Ni-Ru system at 873 K, and the phases present in these assemblages confirm the existence of this phase boundary.

(5) The fact that several Allende opaque assemblages all give temperatures of ~ 770 K and three Leoville assemblages all give temperatures of ~ 873 K supports the suggestions of Blum et al. [2] that opaque assemblages are not pristine high-temperature condensates, that they equilibrated at relatively low temperatures, and that final equilibration was post-accretionary.

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