

THE GEOCHEMICAL BEHAVIOR OF REFRACTORY NOBLE METALS AND LITHOPHILE TRACE ELEMENTS IN CAI'S

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Many CAI's are depleted in the refractory noble metals (RNM: Re, Ru, Os, Rh, Ir, Pt) and some of the lithophile refractory trace elements (LRTE: transition metals, actinides, and REE). The REE also have highly-fractionated Group II patterns in these inclusions, which are usually spinel-rich [1-3]. These depletions and fractionations are understood to result from the physical fractionation of several highly-refractory trace phases during condensation in a hot solar nebula. Variations in elemental ratios among LRTE demonstrate that more than one carrier was fractionated: perovskite, hibonite, and melilite are popular candidates [1,4-7].

In CAI's that do not have Group II REE patterns, refractory trace elements of all geochemical affinities are (fairly) uniformly enriched to ~20X chondritic levels [3,6]. The RNM are concentrated in two different trace constituents of these inclusions: Fremdlinge, which are complex, multiphase aggregates of tiny metal, sulfide, oxide, phosphate, and silicate grains; and rounded Pt-metal nuggets [8]. Some Fremdlinge have been interpreted as aggregates of presolar dust grains; Pt-metal nuggets are usually interpreted to be one of the first of the highly-refractory trace phases that condensed in the solar nebula [8,9]. Pt-metal nuggets and Fremdlinge do not occur in Group II CAI's, whose RNM-depletions could have been caused by the loss of similar objects. LRTE also occur in Fremdlinge: Zr, Y, Nb, Sc, Ta, Th, U, and the REE are enriched in oxide phases (e.g., niobates, baddeleyite) that seem to have been mechanically mixed with the Pt-metal, sulfide, and FeNi-metal grains [8].

An unusual geochemical affinity is also observed in some Pt-metal grains in Fremdlinge, and in larger Pt-metal nuggets: metallic Zr, Nb, and Ta are alloyed with RNM [8,10,11]. This "puzzling" observation can be explained by thermodynamic calculations based on the Engel-Brewer correlation [12] between electronic configurations and phase stabilities of alloys, which illustrate that ZrPt₂, NbPt₂, HfPt₂, and TaPt₂ are stable relative to their respective oxides at f_{O₂} values applicable to the solar nebula. URh₂ is stable relative to UO₂, but only at T > ~1600 K. Y-, REE-, Th-, and Pu-noble metal alloys are unstable under these conditions (Fig. 1).

These data and other factors, such as the extremely small activity coefficients for Zr in noble metals (Table 1), which strongly favor the formation of Zr-noble metal alloys; the exceptional stability of a large number of Zr alloys with Re, Ru, Os, Rh, and Ir [12]; and the stability of other Hf-, Nb-, and Ta-noble metal alloys [12] lead us to the following assertions: (1) metallic Zr, Nb, and Ta observed by [8,10,11] are due to the formation of stable solutions in and/or alloys with RNM (predicted by the Engel-Brewer correlation [12]) that did not require highly-reducing conditions for their formation. (2) Metallic Hf and U may also be present in RNM alloys. (3) The formation of stable U-RNM alloys (but not Th- or Pu-RNM alloys) is a potential mechanism for actinide fractionation based on fractionating metallic and non-metallic carriers, rather than on the basis of the relative volatility of their oxides during condensation [16]. (4) We predict that metallic Y and REE are absent from Pt-metal nuggets and grains because they do not form stable RNM alloys under nebular conditions.

We suggest three possible models to interpret the geochemical behavior of LRTE and RNM in CAI's. The first model can be applied to condensation at high temperatures. Zr is too abundant to have completely condensed alloyed with the RNM (Table 2), but a significant amount of Nb, Hf, U, and Ta could have condensed as metals. We suggest that some of these LRTE (supposedly dissolved in perovskite, spinel, hibonite, melilite, and other major CAI phases) may actually be metals alloyed with sub-microscopic Pt-metal inclusions, rather than oxides in solid solution in them ([18] inferred that sub-microscopic Pt-metal inclusions in Ti-Al-pyroxene and melilite in a Leoville Type B CAI account for a larger proportion of the RNM in the CAI than larger Pt-metal nuggets).

The second model demonstrates how (refractory) chemical fractionations could have occurred in a cold solar nebula, as a result of differences in the physical properties of interstellar dust grains [19,20], and how the loss of a single constituent could have caused correlated LRTE and RNM depletions. In this model, LRTE and RNM condensed as dust grains from hot vapors in extrasolar environments, and aggregated into Fremdlinge before or during the early stages of collapse of the solar nebula [8]. Metal/silicate fractionation in the nebula separated metal-rich Fremdlinge from ordinary interstellar dust. Group II CAI's formed from Fremdlinge-depleted interstellar dust. The tiny (~1 μ g) inclusion analyzed by [11], which has refractory trace-element enrichments and fractionations that are complementary to those in Group II CAI's, would have formed from the Fremdlinge-rich dust component. [This inclusion does contain a Fremdlinge.] A chemical property of Group II CAI's that supports models of cold chemical fractionation is the fact that RNM and non-refractory Pd are depleted, but unfractionated, in Group II CAI's [3] (in all other chemical classes of CAI's, Pd is depleted relative to the RNM). If the RNM had been lost at high temperatures, then there would also have to be a second fractionation at much lower temperature (<1200 K [21]), after Pd condensed, that coincidentally removed the same fraction of Pd. We believe a simpler explanation is that all of the Pt-group metals were lost in a single, low-temperature fractionation.

The third model involves the formation of CAI's by the evaporation and melting of interstellar dust aggregates [20,22]. The primitive(?) Pt-metal grains in Fremdlinge are usually considerably smaller than Pt-metal nuggets. Micron-sized Pt-metal nuggets in Group I CAI's (which are Ca,Al-rich chondrules [3]) may have formed from sub-micron presolar metal grains during the evaporation and melting of interstellar dust aggregates, rather than as nebular condensates. The chondritic Pt-metal ratios observed in some Pt-metal nuggets [8,9] could have been restored by the combining of many smaller, fractionated [8] Pt-metal grains. During this process, LRTE dissolved in silicates and oxides also could have formed the metallic alloys observed in Pt-metal nuggets [8,10,11].

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Table 1. Activity coefficients (γ) of Zr in RNM [12].

RNM	$\log_{10}\gamma$
Ru	-3.4
Rh	< -7
Ir	< -7
Pt	< -12

Table 2. LRTE and RNM abundances [17].

(Si = 10^6)	
Sc	31
Zr	12
Y	4.8
REE	4.3
Nb	0.9
Hf	0.17
Th	0.045
U	0.027
Ta	0.020
Ru	1.9
Pt	1.41
Ir	0.72
Os	0.69
Rh	0.40
Re	0.05
($\Sigma = 5.2$)	

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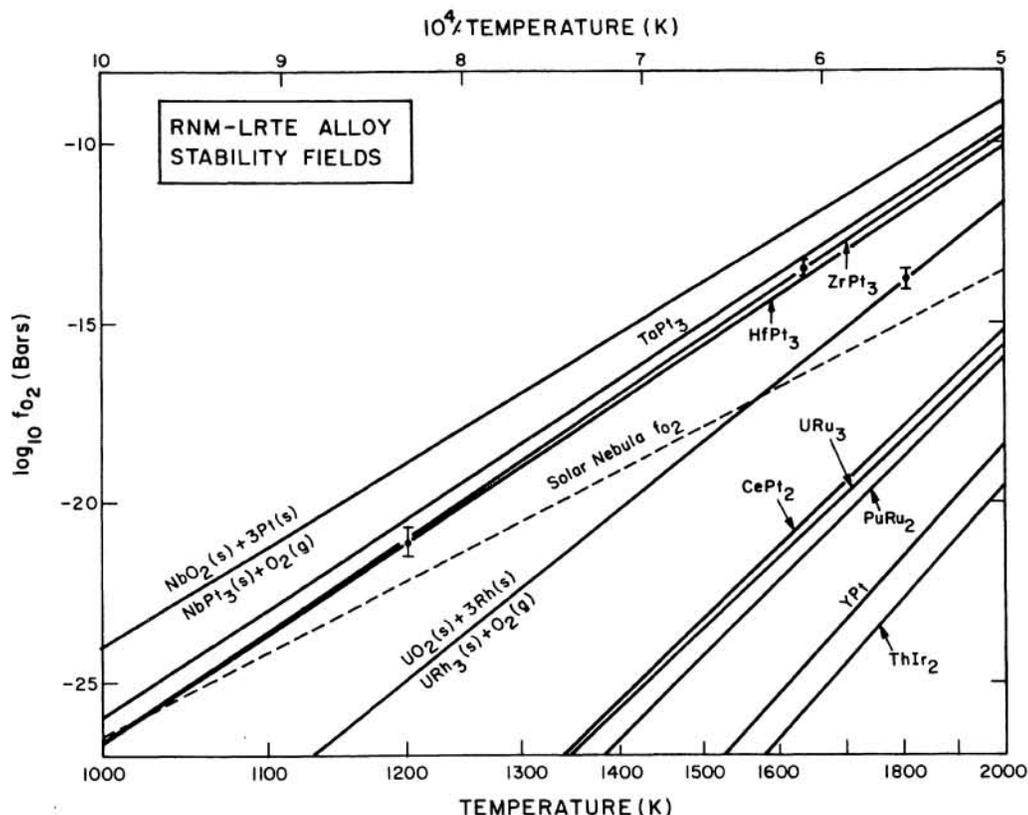


Figure 1. Stability fields of RNM-LRTE alloys. The solid lines (calculated from data in [12-15]) represent reactions such as: $ZrPt_3(s) + O_2(g) \rightarrow ZrO_2(s) + 3Pt(s)$. The RNM-LRTE alloy + O_2 are stable below the solid line; the LRTE oxide + unalloyed RNM are stable above the line. Dashed line: f_{O_2} for a solar-composition nebula at $p = 10^{-3}$ bar. Error bars show the uncertainty in the stability fields.

References: [1] Grossman L. and Ganapathy R. (1976b), *GCA* **40**, 967-977. [2] Mason B. and Martin P.M. (1977), *Smithson. Contrib. Earth Sci.* **19**, 84-95. [3] Mason B. and Taylor S.R. (1982), *Smithson. Contrib. Earth Sci.* **25**. [4] Boynton W.V. (1975), *GCA* **39**, 569-584. [5] Davis A.M. and Grossman L. (1979), *GCA* **43**, 1611-1632. [6] Grossman L. and Ganapathy R. (1976a), *GCA* **40**, 331-344. [7] Davis A.M. et al. (1978), *Proc. 9th LPSC*, 1235-1247. [8] El Goresy A. et al. (1978), *Proc. 9th LPSC*, 1279-1303. [9] Blander M. et al. (1980), *GCA* **44**, 217-223. [10] Dominik B. et al. (1978), *Proc. 9th LPSC*, 1249-1266. [11] Palme H. et al. (1982), *EPSL* **61**, 1-12. [12] Brewer L. and Wengert P.R. (1973), *Met. Trans.* **4**, 83-104. [13] Meschter P.J. and Worrell W.L. (1977), *Met. Trans.* **8A**, 503-509; Wijbenga G. and Cordfunke E.H.P. (1982), *J. Chem. Thermo.* **14**, 409-417. [14] *JANAF Tables* (and supplements), Dow Chem. Co. [15] Ackermann R.J. and Chandrasekhariah M.S. (1974), *Thermodynamics of Nuclear Materials II*, 3-26; Schneider K.A. Jr., Kippenhan N. and McMasters O.D. (1973), *Rep. 15-RIC-6*, REIC. [16] Boynton W.V. (1978), *EPSL* **40**, 63-70. [17] Cameron A.G.W. (1982), *Essays in Nuclear Astrophysics*, 23-43. [18] Palme H. and Wlotzka F. (1979), *Meteoritics* **14**, 508-511. [19] Clayton D.D. (1980), *EPSL* **47**, 199-210. [20] Wood J.A. (1981), *EPSL* **56**, 32-44. [21] Grossman L. and Larimer J.W. (1974), *Rev. Geophys. Space Phys.* **12**, 71-101. [22] Wark D.A. and Lovering J.F. (1982), *GCA* **46**, 2581-2594.