

## THE VARIATION OF Zn CONTENT IN SPINEL GROUP MINERALS AND DAUBREELITES OF PRIMITIVE ACHONDRITES

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**Abstract:** We have studied the Zn content of spinel group mineral and daubreelite in primitive achondrites in order to clarify how the content of Zn, a moderately volatile element, reflects their formation process. Primitive achondrites have achondritic texture and chondrite-related chemistry and mineralogy. Because of these characteristics, primitive achondrites are thought to represent the transition from chondrites to achondrites.

We have compared the Zn content in spinel group minerals of primitive achondrites with those of chondrites and ureilites. Although Zn is a moderately volatile element, the Zn content in spinel group mineral of primitive achondrites, ureilites and metamorphosed chondrites is higher than unmetamorphosed chondrites. This fact suggests that high Zn content in spinel group mineral of primitive achondrites may result from secondary crystallization or reequilibration of spinel mineral from a sulfide melt containing Cr, Mn and Zn which was partially melted during thermal metamorphism.

We also found that the Zn content in spinel group minerals decreases from primitive achondrites and ureilites to HED and Martian meteorites. We suggest that Zn was significantly volatilized from completely molten magma in these meteorites.

We found that spinel group minerals and daubreelites appear to be the major reservoir of Zn in most meteorites. Zn may be preferentially retained in the tight spinel structure.

### 1. Introduction

Until now, few researchers have studied Zn in meteorites (*e.g.*, KALLEMEYN and WASSON, 1986; NISHIMURA and SANDWELL, 1964; PALME *et al.*, 1988); the following facts are known. 1) Bulk Zn content in chondrules is lower than matrix in some little-metamorphosed chondrites like Semarkona, Chainpur and so on (KALLEMEYN and WASSON, 1986). 2) Chondrites have significant Zn content in their silicates, while achondrite silicates do not contain Zn (NISHIMURA and SANDWELL, 1964). 3) The depletion patterns of S and Zn in meteorites are very similar, although the extent of fractionation is significantly greater for Zn. A systematic study about Zn for individual mineral phases has not been conducted yet. This paper will begin to address this gap.

At first, we will explain the geochemical properties of Zn and the reason why we paid attention to the Zn content in spinel group minerals. Zn is one of the moderately volatile elements such as S, Na, and K (PALME *et al.*, 1988). The 50% condensation

temperature of Zn is rather low (660K; WASSON, 1985) indicating that Zn is a volatile element. KRAUSKOPF (1979) noted that meteorites contain 115 ppm Zn in metal, 1530 ppm in sulfides, 76 ppm in silicates and that ore melts contain 8 ppm Zn in metal, 16800 ppm in sulfides, 3700 ppm in silicates. NISHIMURA and SANDWELL (1964) found that in the most abundant major type of meteorite (ordinary chondrite) very little Zn is contained in sulfide or metal, which seems a direct contradiction with the data of KRAUSKOPF (1979). Zn behavior in meteorites is still controversial. Under the reducing conditions which prevailed during the formation of enstatite chondrites, Zn is chalcophile and mainly sited in sphalerite (ZnS). On the other hand, other chondrites and achondrites usually do not contain sphalerite. Therefore, while Zn is chalcophile in behavior under reducing conditions as for enstatite chondrite, it is not chalcophile in other meteorites. The crystal chemical behavior of Zn is mainly controlled by the similarity in ionic radii between divalent Zn and the cations of the magnesium-iron group, especially Fe (GOLDSCHMIDT, 1954).

Our study already showed that Zn is contained in Cr-rich spinel grains in the LEW 88774 ureilite (CHIKAMI *et al.*, 1997a). High Zn chromite was also found in the shock recrystallized LL7 chondrite (TAKEDA *et al.*, 1984). YABUKI *et al.* (1983) also found the high Zn content (up to 2.3 wt% ZnO) and the positive clear-cut relationship between Zn and Al contents of the chromites in many chondrules in L3, L4 and L5 chondrites and some LL's. From these studies, we think that Zn may be commonly present in spinel group minerals and that the particular Zn content in spinel group minerals may reflect the thermal history of each meteorite because of the volatile behavior of Zn. We became interested in spinel group minerals in primitive achondrites because primitive achondrites are thought to be a transition from primitive meteorites to differentiated meteorites such as LL7 and LEW88774 ureilite (TAKEDA *et al.*, 1984; CHIKAMI *et al.*, 1997a). In this study we focus on the Zn content of spinel group minerals in primitive achondrites. In this paper we use the term "spinel group minerals" as spinel-structured minerals which include chromite, magnesiochromite and Cr-rich spinel.

"Primitive achondrites" is a term for the rare meteorites that have achondritic texture and chondrite-related chemistry (PRINZ *et al.*, 1980). Members of this group include acapulcoites, lodranites, winonaites and silicate inclusions in IAB and IIICD irons. Acapulcoites are equigranular aggregates of major fine-grained orthopyroxene and olivine with minor amounts of FeNi metal, plagioclase, troilite, augite, chromites and phosphates. They appear to be extensively recrystallized chondrites. Lodranites are essentially coarse-grained orthopyroxene-olivine rocks and are typically poor in plagioclase and phosphates. Winonaites were defined originally by PRINZ *et al.* (1980, 1983) and mineral assemblage of winonaites is similar to acapulcoites although winonaites are generally more reduced than acapulcoites (KIMURA *et al.*, 1992). Silicate inclusions in IAB irons resemble winonaites compositionally and mineralogically. The oxygen isotopic compositions indicate that the parent asteroid of the acapulcoites/lodranites group is different from the winonaites and silicate inclusions of the IAB iron group parent body (CLAYTON *et al.*, 1992).

Primitive achondrites may contain evidence of the processes responsible for the transition from chondrites to achondrites because they have both chondritic and achondritic characteristics. Accordingly, we studied how the Zn content of spinel

group minerals and daubreelite, which is a thiospinel, in primitive achondrites reflect their formation history and compared them to those in other meteorites.

## 2. Sample and Experimental Techniques

In order to understand Zn behavior within daubreelite and chromite in primitive achondrites, we studied acapulcoites (Acapulco, Allan Hills (ALH)-78230, Yamato (Y)-8307), lodranites (Y-8005, Gibson, Y-791491), silicate inclusions in IAB irons (Caddo County and Y-791058), and winonaites (Y-75305 and Y-74025) containing both daubreelite and chromite. We also performed mineralogical studies of an H7 chondrite (Y-75008), a LL7 chondrite (Y-74160), an ureilite (LEW88774), 4 eucrites (Asuka (A)-881388, A-881394, Y-790447, Y-75210), a diogenite (Y-74013) and a SNC meteorite (Zagami) to understand systematically the geochemical and crystal chemical behavior of Zn from chondrite to achondrite.

Polished thin sections (PTSs) of ALH-78230 and Y-8307 (acapulcoites), Y-791491 and Y-8002 (lodranites), Y-75305,52-2 and Y-74025,52-4 (winonaites) and Y-791058 (IAB) were supplied from National Institute of Polar Research (NIPR). PTSs of Acapulco, Gibson and Caddo County were supplied from the meteorite collection of the Planetary Materials Database of University of Tokyo.

We studied each sample using an optical microscope, a scanning electron microscope and electron probe microanalyzers (JEOL EPMA JCXA-733 at the Ocean Research Institute, University of Tokyo and JEOL EPMA JCXA 733-mkII and JEOL EPMA JCXA-8900L at the Geological Institute, University of Tokyo). We measured 13 elements (Si, Ti, Al, Mn, Fe, Mg, Ca, Na, K, Cr, V, Ni and Zn) in chromites, using an accelerating voltage of 15 kV and a beam current of 12 nA. We measured 9 elements (Co, Fe, Ni, Cr, P, S, Si, Mn and Zn) in daubreelite, using an accelerating voltage of 25 kV and a beam current of 20 nA. Counting times at peak wavelengths were 10 s. Counts were accumulated 6 times. The background intensity was measured for each element at both sides of the peak wavelength. In these analysis, the detection limit for ZnO in spinel and Zn in daubreelite is 0.015 wt%.

## 3. Results

### *Acapulcoites*

ALH-78230 is an acapulcoite (YUGAMI *et al.*, 1994) and consists mainly of orthopyroxene, olivine, plagioclase, troilite, FeNi metal and augite. Chromites contain 1.26–1.45 wt% (average; 1.3 wt%) ZnO (core content).

Acapulco is slightly coarser grained than ALH-78230, and consists of major orthopyroxene, olivine, plagioclase, troilite, FeNi metal and augite. There are oriented dusty inclusions in orthopyroxene grains. Qualitative analysis suggest that these inclusions are FeNi metal. Chromites in Acapulco contain 0.85–1.66 wt% (average; 1.3 wt%) ZnO (core content). Chromites in contact with metal and troilite display a variety of zoning patterns of Cr, Al, Ti and Zn (EL GORESY and JANICKE, 1995). The Zn concentration which these investigators report are almost same as our data. ZIPFEL *et al.* (1995) gave a slightly lower result (0.88 and 0.91 wt%) for Zn in chromite of

acapulcoite.

Y-8307 has been described as a primitive achondrite (YANAI and KOJIMA, 1995) but has not been described in detail. It is slightly coarser than Acapulco and ALH-78230, with an average grain size of about 0.3 mm. It consists mainly of orthopyroxene, olivine, plagioclase, FeNi metal, augite and troilite. Chromites in Y-8307 contain 1.20–1.95 (average; 1.7 wt%) ZnO (core content).

#### *Lodranites*

The Y-791491 lodranite contains major coarse-grained olivine and orthopyroxene, variable amounts of troilite and FeNi metal, and minor plagioclase (TAKEDA *et al.*, 1994). Chromites coexisting with metal and silicates contain 0.58–0.65 wt% (average; 0.6 wt%) ZnO (core content).

The texture of Gibson is different from those of common lodranites. It contains considerable amounts of augite and plagioclase (YUGAMI, 1996). It consists mainly of orthopyroxene, olivine, FeNi-metal, augite, plagioclase and with small amount of troilite. Chromites in Gibson contain 0.15–0.23 wt% (average; 0.2 wt%) ZnO (core content).

Y-8002 is coarse-grained (0.5–2 mm in size). The same PTS was previously investigated by NAGAHARA (1992). It consists mainly of orthopyroxene, olivine, FeNi-metal, and plagioclase with small amount of troilite. Magnesiochromites in Y8002 contain 0.50–0.51 wt% (average; 0.5 wt%) ZnO (core content).

#### *Silicate inclusions in IAB irons*

Silicate inclusions in the Caddo County IAB iron meteorite (TAKEDA *et al.*, 1994) contain chromite grains coexisting with troilite and metal. These chromite grains contain the highest ZnO content (2.11–2.43 wt%, average; 2.2 wt%) (core content) among samples we analyzed in this study.

Y-791058 consists mainly of orthopyroxene, olivine, plagioclase, FeNi-metal and troilite. Chromites in Y-791058 contain 2.1–2.4 wt% (average; 2.2 wt%) ZnO (core content).

#### *Winonaites*

Y-75305,52-2 is a winonaite and consists of major FeNi metal, orthopyroxene and plagioclase and minor olivine, augite and troilite (KIMURA *et al.*, 1992; YUGAMI, 1996). Y-75305 contains daubreelite, chromite, apatite and schreibersite as accessory minerals. Daubreelites contain only small amounts of Zn (0.03–0.07 wt%, average; 0.06 wt%) (core content), while chromites contain much higher amounts (0.99–1.99 wt%, average; 1.6 wt%) (core content). These data are consistent with those of KIMURA *et al.* (1992).

Y-74025 is also a winonaite. Y-74025,52-2 was previously investigated by KIMURA *et al.* (1992). We analyzed PTS, Y-74025,52-4. The sample we studied consists of major orthopyroxene, olivine, plagioclase and troilite and minor FeNi metal and augite. It also contains schreibersite and daubreelite as accessory minerals. The Zn content of daubreelites is 0.11–0.15 wt% (average; 0.13 wt%) (core content), slightly higher than in Y-75305,52-2. Chromites were not found in Y74025,52-4, but KIMURA *et al.* (1992)

reported 1.28 wt% ZnO in chromites in Y-74025,52-2.

#### 4. Discussion

##### 4.1. Zn in spinel structure

Spinel-structured minerals in primitive achondrites are chromites/magnesiochromite and daubreelite. All 4 kinds of primitive achondrites contain chromite/magnesiochromite, and winonaites contain both chromite and daubreelite. Daubreelite,  $\text{FeCr}_2\text{S}_4$ , which is a thiospinel, is found in only highly reduced and sulfur-rich meteorites (RAMDOHR, 1973). Daubreelite is a common component of many troilite nodules in iron meteorites. Both chromite/magnesiochromite and daubreelite have the normal spinel structure in which 8 cations occupy the eight tetrahedral sites, while 16 cations occupy the 16 octahedral sites. Zn occupies the tetrahedral sites. Because of its electronic structure, Zn has a strong tendency towards tetrahedral coordination although ionic size alone would favor octahedral coordination (GOLDSCHMIDT, 1954). Because of this similarity in structure, it is not surprising that Zn can be incorporated into both minerals.

ZIPFEL *et al.* (1995) showed that chromites in Acapulco contain a much higher Zn content compared with that for orthopyroxene, olivine and troilite grains. We have also confirmed that Zn content of pyroxene, olivine, troilite and FeNi metal in primitive achondrites which we have used is under the detection limit of EPMA. Y-74160 is an LL7 chondrite with a bulk Zn concentration at CI levels, whereas other volatile, chalcophile elements are depleted (TAKEDA *et al.*, 1994). Many studies (*e.g.*, BINZ *et al.*, 1976; KALLEMEYN and WASSON, 1986; KALLEMEYN *et al.*, 1989) indicate that bulk-rock Zn remains approximately constant during metamorphic alternation of chondrites from type 3 to type 6. Zn behavior may be different from those of other volatile elements. Chromite in the Y-74160 LL7 chondrite contains 0.6 wt% ZnO and other minerals contain Zn under the detection limit (CHIKAMI *et al.*, 1997a), although the modal abundance of chromite in Y-74160 is only 3% (TAKEDA *et al.*, 1984). LEW 88774 is an unusual ureilite containing spinels. Bulk Zn content in LEW88774 is at the CI level (KALLEMEYN and WARREN, 1994). Cr-rich spinels in LEW88774 also contain ZnO up to 0.6 wt% while other minerals contain Zn under the detection limit. The modal abundance of spinel in the LEW88774 ureilite is 6% (WARREN and KALLEMEYN, 1994; KALLEMEYN and WARREN, 1994; PRINZ *et al.*, 1994; CHIKAMI *et al.*, 1997a). The Cr-rich spinel mineral in this ureilite are the reservoir of almost all the Zn in this sample (CHIKAMI *et al.*, 1997a).

We suggest that spinel group minerals are the major reservoir of Zn in LL7 chondrite except enstatite chondrites, primitive achondrites and ureilites.

##### 4.2. Zn behavior from unmetamorphosed chondrites to primitive achondrites

It has been known that chromites from carbonaceous chondrites generally have ZnO above the detection limit (0.015 wt%) of EPMA, and that up to 2–3 wt% ZnO can be concentrated in chromite in the L and LL chondrites (JOHNSON and PRINZ, 1990). JOHNSON and PRINZ (1990) reported that among CO3 carbonaceous chondrites, chromites in ALH-77307 (3.0) and Kainsaz (3.1) have ZnO below the detection limit of 0.04

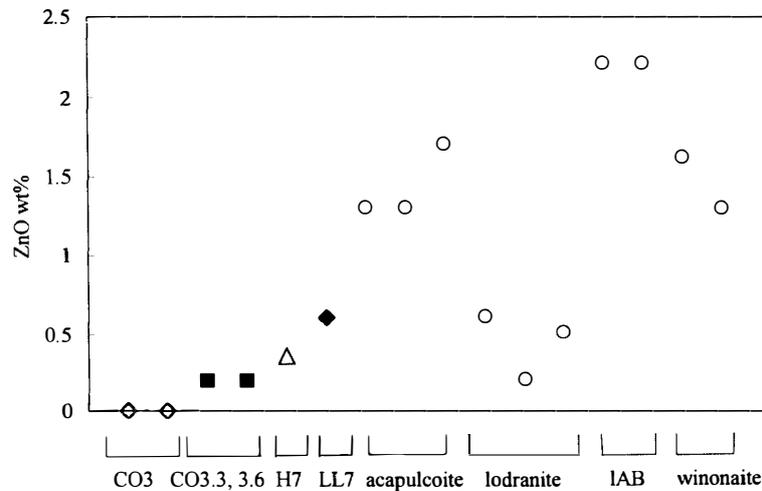


Fig. 1. ZnO wt% in spinel from CO3 chondrite to primitive achondrite. ZnO wt% of spinel in CO3 chondrite is under the detection limit of EPMA. Data of CO3 and CO3.3, 3.6 from JOHNSON and PRINZ (1990). On x axis, we ordered the meteorites according to the degree of differentiation. Errors ( $\pm\sigma$ ) based on counting statistics are within the size of markers.

wt%, whereas chromites in Ornans (3.3) and Warrenton (3.6) contain 0.1–0.3 wt% ZnO. Similarly, non-reequilibrated chromites in Semarkona (LL3.0) have Zn below detection, whereas chromites in virtually all LL and L chondrites of higher petrographic type contain >0.1 wt% ZnO. Similarly we found that the ZnO content of chromites in the Y-75008 H7 chondrite is 0.3–0.4 wt% and that in the Y-74160 LL7 chondrite is 0.6 wt% (0.2–2.2 wt%) (TAKEDA *et al.*, 1984; CHIKAMI *et al.*, 1997a,b). We summarized the results of Zn content in spinel group minerals from unmetamorphosed chondrites to primitive achondrites in Fig. 1. PALME *et al.* (1981) compared the bulk Zn content of H7 chondrites with Acapulco, and found that Acapulco contains higher Zn contents than H7 chondrites. JOHNSON and PRINZ (1990) suggested that the high Zn contents in chromites of thermally metamorphosed chondrites may result from reequilibration of the chromites with other minerals.

TAKEDA *et al.* (1994) suggested that the complex textures of chromites in lodranites with arms filling the interstices of silicate grains show that these chromites were formed by a similar process to that of metal formation (*i.e.*, migration of materials along grain boundaries, probably as a liquid phase). On the other hand, chromites in diogenite show different textures and isolated euhedral octahedral shapes. This shape of chromite in diogenite means that chromites were crystallized from molten magma. ZIPFEL and PALME (1993) also suggested that the different Cr content in chromite among acapulcoites indicates mobilization of chromite. We suggest that the high Zn contents in chromites/magnesiochromites of primitive achondrites may result from secondary crystallization or reequilibration of chromites from a sulfide melt containing chalcophile Cr, Mn and Zn which was partially melted during thermal metamorphism (CHIKAMI *et al.*, 1997b).

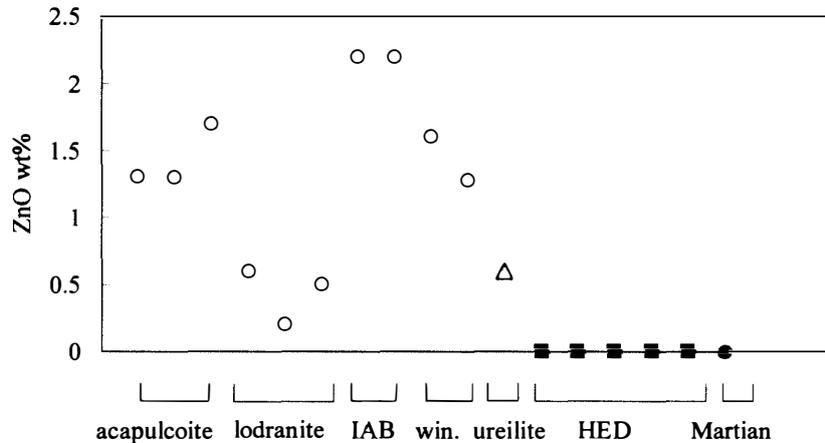


Fig. 2. ZnO wt% in spinel from primitive achondrite to HED and Martian meteorites. ZnO wt% of spinel in HED and Martian meteorites is under the detection limit of EPMA. Win. is winonaite. On x axis, we ordered the meteorites according to the degree of differentiation. Errors ( $\pm\sigma$ ) based on counting statistics are within the size of markers.

#### 4.3. Zn behavior from primitive achondrites to achondrites

We compared the Zn content in primitive achondrites with that in other achondrites (Fig. 2). LEW88774 is a ureilite, which are a class of achondrites with both chondritic and achondritic character (WARREN and KALLEMEYN, 1994). This sample contains Cr-rich spinel with significant Zn content (0.6 wt%), like spinel group minerals in primitive achondrites (CHIKAMI *et al.*, 1997a). In ureilites the major host carriers for Zn are olivine and/or pyroxene, since spinel group minerals usually is rare (GOODRICH, 1992). Sodium is less volatile than Zn but is strongly depleted in ureilites. This observation suggests that Na is depleted during partial melting which causes depletion of plagiophile elements in ureilites, but Zn can be retained in spinel group minerals which were produced from the partial melt or reequilibrated with other minerals during partial melting. On the other hand, eucrites (A-881388, A-881374, Y-790447, Y-75210), diogenite (Y-74013) and the one SNC meteorite (Zagami) investigated do not contain detectable Zn in their spinel group minerals (CHIKAMI *et al.*, 1997b,c).

The differentiated meteorites such as eucrites, diogenites and SNC meteorites are strongly depleted in Zn. These samples crystallized from molten magma that was depleted in many volatile elements, such as Zn and Na long before crystallization of spinel group minerals. Alternatively, the parent bodies for these meteorites may have been originally depleted in Zn (*i.e.* during accretion).

The retention of significant Zn in primitive achondrites suggests they have not undergone a large thermal event of sufficient intensity to volatilize all Zn like HED and Martian meteorites.

#### 4.4. Zn behavior among primitive achondrites

We summarized the results of Zn content in spinel group minerals among various primitive achondrites (Table 1 and Fig. 3). We found that ZnO contents in chromites

Table 1. Average chemical compositions of spinel group minerals in primitive achondrites.

	Acapulcoites			Lodranites			IAB		Winonaite
	ALH-78230	Aca.	Y-8307	Y-791491	Y-8002	Gib.	Cadd.	Y-791058	Y-75305
Na <sub>2</sub> O	-	0.05	0.04	-	-	-	-	0.04	0.05
MgO	6.79	6.65	6.79	5.59	15.8	14.3	8.14	7.40	14.2
SiO <sub>2</sub>	0.11	0.10	0.08	0.02	0.06	0.10	0.04	0.20	0.20
Al <sub>2</sub> O <sub>3</sub>	6.75	5.03	6.40	3.99	4.84	9.83	1.35	2.66	8.20
K <sub>2</sub> O	-	-	-	0.03	-	-	-	-	-
CaO	-	0.03	-	0.02	0.03	-	-	-	-
TiO <sub>2</sub>	1.34	1.24	1.22	0.85	0.81	0.80	0.35	0.34	1.48
Cr <sub>2</sub> O <sub>3</sub>	59.7	63.2	61.4	63.4	68.8	62.6	69.0	63.6	61.8
MnO	1.25	1.85	1.51	1.67	1.33	2.31	5.35	3.98	1.42
FeO	22.0	20.6	20.5	23.1	7.12	9.89	13.1	17.6	9.76
NiO	-	-	-	0.03	-	-	-	0.04	-
ZnO	1.27	1.34	1.77	0.58	0.51	0.23	2.19	2.24	1.57
Total	99.2	100.1	99.7	99.3	99.3	100.1	99.5	98.1	98.7

Aca: Acapulco, Gib: Gibson, Cadd: Caddo County, IAB: silicate inclusion in IAB iron,  
 -: under the detection limit, which are 0.01 for Na<sub>2</sub>O, 0.02 for K<sub>2</sub>O, 0.01 for CaO, 0.02 for NiO.

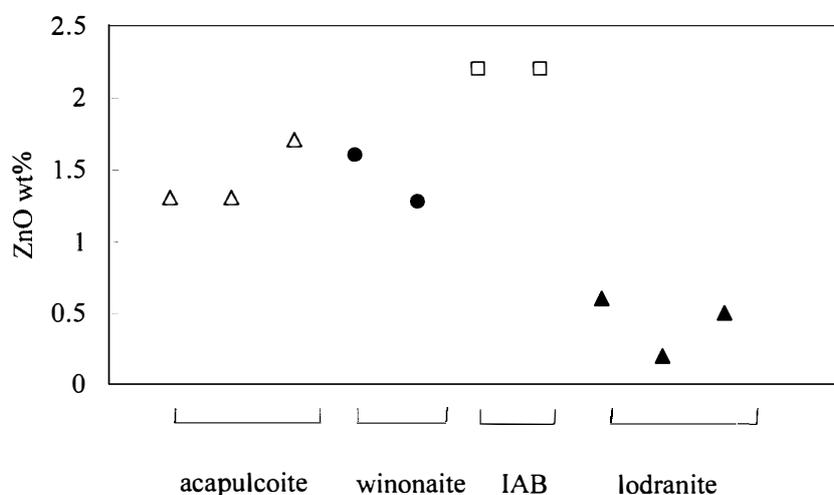


Fig. 3. ZnO wt% in spinel among primitive achondrites (acapulcoite, winonaite, silicate inclusion in IAB iron and lodranite). Errors ( $\pm\sigma$ ) based on counting statistics are within the size of markers.

of acapulcoites are higher than chromites/magnesiochromites of lodranites in this study and for that of TAKEDA *et al.* (1994) (MAC88177, Y-74357, EET84302). This fact is also consistent with the Zn content in chromites of other lodranites which were analyzed by TAKEDA *et al.* (1994). As we explained in the Introduction, lodranites have larger grains than acapulcoites and are typically poorer in plagioclase and phosphates than acapulcoites. TAKEDA *et al.* (1994) and MCCOY *et al.* (1997) proposed that heating of the acapulcoite/lodranite parent body to temperatures between 1050–1200°C resulted in

formation of (Fe, Ni)-FeS and basaltic partial melts and produced the lodranites. The acapulcoites are samples of materials heated to lower temperatures, and thus, experienced lower degrees of partial melting (McCoy *et al.*, 1997). McCoy *et al.* (1997) suggested that lodranites reached higher peak temperature than acapulcoites. A higher peak temperature would have permitted melt migration explaining the low abundance of plagioclase and phosphates in lodranites. YUGAMI (1996) proposed a model for the formation process of primitive achondrites in which melt migrated by a local segregation mechanism. Chromites in lodranites have been proposed to have crystallized from a partial melt (TAKEDA *et al.*, 1994). Zn might have been lost during such episode. Perhaps during this melt migration the grain sizes increased from acapulcoites to lodranites. During such local melt migration, volatile elements such as Zn may be depleted. This is consistent with the difference of bulk Zn content between acapulcoites and lodranites (ZIFFEL and PALME, 1993). As a result, lodranites contain less Zn in spinel group minerals than acapulcoites.

#### 4.5. Zn behavior between chromite and daubreelite

EL GORESY (1967) showed that the daubreelites coexisting with troilite and sphalerite in the Odessa IAB iron meteorites display variable chemical composition with strong fluctuations in their Zn content. On the other hand, troilites coexisting with daubreelite do not contain detectable Zn. Zn contents as high as 8 wt% were recorded in several grains of daubreelite in the Odessa iron meteorite (EL GORESY, 1967), while the Zn content in chromites is 1.39 wt% (BUNCH *et al.*, 1970). These studies indicate that Zn is not only present in significant amounts in sphalerites and chromites, but also in daubreelites.

We summarized the results of Zn content in daubreelite in primitive achondrites (Table 2) and compared this result with the Zn content of chromites in primitive achondrites. Using Zn contents and modal abundances of chromite and daubreelite, we calculated roughly how much of the bulk Zn in the Y-74025 winonaite is contained in each mineral. Almost 70% of the Zn is contained in chromite and about 15% in

Table 2. Average chemical compositions of daubreelites in winonaite.

	Y-74025	Y-75305
Co	0.02	-
Fe	18.0	18.5
Ni	-	0.02
Cr	35.0	35.1
P	-	-
S	44.3	44.0
Si	-	-
Mn	1.01	1.39
Zn	0.13	0.06
Total	98.5	99.1

-: under the detection limit, which are 0.01 for Co, 0.01 for Ni and 0.03 for P and Si.

daubreelite, although modal abundances of both chromite and daubreelite are very low (chromite; under 0.2 vol%, daubreelite; 0.51–0.7 vol%) (KIMURA *et al.*, 1992; YUGAMI, 1996). This fact suggests that chromite might be more effective in retaining Zn than daubreelite in these winonaites. In order to explain the different Zn behavior between chromite and daubreelite in winonaites and iron meteorites, we have to think several possibilities. It might be possible that the precursor material of daubreelite is different from chromite. Different Zn content in daubreelite and chromite depends on how much Zn was contained in the precursor material of each mineral. To confirm this possibility, further isotopic study for each mineral will be needed. Assuming that chromite and daubreelite in winonaites and iron meteorites were produced from the same precursor material, we can propose two alternative possibilities that control whether Zn is preferentially retained in chromite or daubreelite. The first possibility is the crystallization order of chromite and daubreelite. For example, daubreelite in primitive achondrites may have formed later during sulfidization, after chromite took up considerable Zn from the primary melt. Alternatively, the partitioning of Zn between daubreelite and chromite could depend on oxygen fugacity. In order to consider which mineral Zn is preferentially retained in chromite or daubreelite, further study will be needed.

## 5. Conclusions

(1) Spinel group minerals appear to be the major reservoir of Zn in most meteorites we have studied.

(2) The Zn content of spinel group minerals in meteorites increases from unequilibrated chondrites and equilibrated chondrites to primitive achondrites or ureilites. The high Zn content in thermally metamorphosed chondrites, primitive achondrites and ureilites may result from secondary crystallization or reequilibration of spinel group minerals.

(3) The Zn content decreases in the order: primitive achondrite and ureilites to HED and Martian meteorites. HED and Martian meteorites crystallized from molten magma that was depleted in many volatile elements. On the other hand, the retention of significant Zn in primitive achondrites and ureilites suggests that they have not undergone a large thermal event such as HED and Martian meteorites.

(4) The Zn content of chromites in acapulcoites is much higher than that in lodranites. It might be caused by the different peak temperature between acapulcoites and lodranites.

## Acknowledgments

We are indebted to the Meteorite Working Group, National Institute of Polar Research and the Planetary Materials Database of University of Tokyo for samples. We thank Mr. O. TACHIKAWA at the Mineralogical Institute, and Mr. H. YOSHIDA at the Geological Institute, University of Tokyo for their technical assistance. We thank Drs. A. EL GORESY, T.J. MCCOY, H. PALME, M. ZOLENSKY, G. MCKAY and K. YUGAMI for helpful discussion. We also thank Drs. M. KIMURA and P.H. WARREN for constructive

reviews. This work was supported by JSPS Research Fellowship for Young Scientists (J.C.)

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*(Received August 31, 1998; Revised manuscript accepted October 26, 1998)*