#### Notes

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# Volatile/mobile trace elements in Karoonda (C4) chondrite

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Abstract--Data for ten volatile/mobile trace elements and non-volatile Co in Karoonda (C4) and in heated primitive chondrites are consistent with the suggestion that Karoonda derives from low-temperature, open-system metamorphism of pristine C3-like material.

#### **INTRODUCTION**

GENETICALLY, carbonaceous chondrites seem the best understood of any chondritic group, their chemical composition and mineralogy generally being consonant with a twocomponent mixing model (cf. ANDERS *et al.*, 1976). Trace elements highly-depleted relative to cosmic or C1 levels in equilibrated ordinary chondrites (cf. ANDERS *et al.*, 1976; BINZ *et al.*, 1976) exhibit trends in carbonaceous chondrites which arc especially significant for this model. In particular, C1:C2:C3 abundance ratios of 1.00:0.51:0.2-0.3 seemingly were established during nebular condensation and subsequent accretion and mixing in different proportions of high- and low-temperature fractions, the latter hosting the highly-depleted and presumably volatile elements.

Continued study of carbonaceous chondrites, particularly of the Vigarano and Ornans sub-groups of C3 chondrites, suggest minor modifications which have been incorporated into this model (cf. ANDERS et al., 1976 for references). For example, volatile elements are depleted to near constant ratios in four C3V and three C30 chondrites suggesting that members of each group accreted at the same temperature; however the excess depletions of Tl in Kaba (C3V) and Cd in four of the seven chondrites are taken, respectively, to reflect Kaba's accretion at slightly higher temperature and incomplete condensation of Cd. ANDERS et al. (1976) note that the latter depletion cannot be due to metamorphism since unreported data for the moremetamorphosed C4-5 chondrites Coolidge and Karoonda show no such excess depletion. ANDERS (private communication) believes that these data for Coolidge and Karoonda fit the two-component model rather well.

All mineralogic/petrologic studies agree that Karoonda is the more heavily metamorphosed of these two C4-5 chondrites. VAN SCHMUS and WOOD (1967) suggest derivation of C4 from C3 chondrites. VAN SCHMUS (1969) noted that both could have been derived from C2 and C3 chondritic material during metamorphism in a parent body (cf. VAN SCHMUS and HAYES, 1974) and McSWEEN (1977a) suggested that C30 chondrites and Karoonda (C4-5) constitute an increasingly metamorphosed suite. According to McSWEEN (1977a) metal equilibration in several C30 chondrites suggest metamorphic temperatures  $\leq 450^{\circ}$ C; more-altered Karoonda experienced a higher temperature which cannot be specified because of the scarcity of metal in it. CLAYTON *et al.* (1977) report oxygen isotopic data indicating concordant equilibration temperatures for plagioclase-olivine and plagioclase-magnetite pairs in Karoonda of 580 and 590°C, respectively.

Recently we found that many highly-depleted trace ele-

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ments---including Ag, Bi, Cd, Cs, Ga, In, Se, Te, Tl and Zn-are mobilized and lost from geologic material (including primitive chondrites) by week-long heating in a low-pressure—initially  $\sim 10^{-5}$  atm H<sub>2</sub>—environment (e.g. IKRAMUDDIN and LIPSCHUTZ, 1975; cf. IKRAMUDDIN et al., 1977). Losses progress in the 400-1000°C range to extremes of 100-fold in many cases and comparison of trace element trends in heated primitive chondrites and their moreevolved congeners indicate that the various chondritic groups reflect substantially different metamorphic histories (cf. IKRAMUDDIN et al., 1976, 1977). Our experiments included two carbonaceous chondrites-Murchison (C2) and Allende (C3V)-which exhibit radically different retentivity trends for volatile trace elements. In view of the consensus that the mineralogy/petrology of Karoonda reflects metamorphism we felt it worthwhile to determine these ten volatile trace elements (and non-volatile Co) in it and to establish whether their trends are consistent with metamorphism. We wish to acknowledge that Anders and coworkers studied this chondrite before we did but we have not seen their data and, apart from Cd, we do not know which elements they measured.

#### EXPERIMENTAL

We prepared duplicate samples of Karoonda for neutron activation by removing potentially contaminated surfaces from a sample (Me-2666) obtained from Dr. E. Olsen of the Field Museum of Natural History. We treated the samples as described by IKRAMUDDIN *et al.* (1976). The accuracy (cf. McSwEEN, 1977a) and precision of our results is quite satisfactory (Table 1). Our analytical techniques have been tested in many previous studies and there seems no reason to doubt their accuracy. Since we compare *our* results for Karoonda, Allende and Murchison, systematic differences should be minimal and, as will be seen, our conclusions would be strengthened were the few prior Karoonda data used (cf. McSwEEN, 1977a).

#### DISCUSSION

We order elements in Table 1 by depletion in Karoonda relative to C1 chondrites and plot these data, those for unheated Allende (IKRAMUDDIN and LIPSCHUTZ, 1975; BART and HUNG, unpublished data) and Murchison, unheated and heated at 500 and 600°C (MATZA and LIPS-CHUTZ, 1977), in Fig. 1. [We include heated Murchison data for illustrative purposes only. We do not imply that Karoonda derives from Murchison-like or even C2 mater-

Table 1. Trace element of	contents i	in K	Caroonda
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	Concentration			Atomic Abundance		
	(1)	(2)	Mean	atoms/	Karoonda/C1 <sup>+</sup>	
	10 <sup>6</sup> Sf atoms					
Co(ppm)	635	637	636±1	1950	0.87	
Ga(ppm)	5.55	5.17	5.36±0.27	13.9	0.32	
Se(ppm)	7.83	7.57	7.70±0.18	17.6	0.27	
Ag(ppb)	60.2	65.2	62.7±3.5	0.105	0.23	
Żn (ppm)	101	102	102±1	282	0.23	
Cs(ppb)	69.9	59.0	64±8	0.088	0 22	
Te(ppb)	912	902	907±7	1.28	0.20	
Cd(ppb)	190	169	180±15	0.289	0.19	
In(ppb)	20.4	23.0	21.7±1.8	0.0341	0.18	
Bi(ppb)	30.3	29.6	30.0±0.5	0.0259	0.18	
Tl(ppb)	25.8	23.8	24.8±1.4	0.0219	0.12	

\* Uncertainties listed are one estimated standard deviation from the mean calculated from the dispersion of the duplicate measurements.

 $\ddagger$  Karoonda abundances derive from the Si datum of WIIK (1969) and C1 abundances are obtained from sources listed in BINZ *et al.* (1974).

ial; merely that Murchison's behavior more nearly should typify that of pristine carbonaceous material than should Allende, which may have been mildly sintered (MATZA and LIPSCHUTZ, 1977; MCSWEEN, 1977b).]

Data for the ten depleted, i.e. volatile, elements  $Ga \rightarrow ln$ in unheated Murchison and Allende clearly accord well with the two-component model (Fig. 1). These elements generally are depleted by constant amounts in each meteorite (cf. ANDERS et al., 1976) and the mean depletion factors,  $0.50 \pm 0.06$  for Murchison and  $0.31 \pm 0.07$  for Allende, suggest that these chondrites represent 50% and 31%, respectively, of low-temperature material of C1 composition and complementary amounts of high-temperature material devoid of volatiles. [Most  $\delta f$  the 23% uncertainty in the mean depletion factor for Allende can be ascribed to Cd, an element well-known for aberrant behavior; omission of this element does not markedly alter the mean  $(0.29 \pm 0.04)$  but reduces the uncertainty nearly to that of Murchison, 12%]

The mean depletion factor of these ten elements in Karoonda,  $0.21 \pm 0.05$ , might be interpreted in a similar fashion as ANDERS (personal communication) suggests. However, by consensus, Karoonda represents a carbonaceous chondrite metamorphosed in either a closed or open system. In the former case volatile trace element contents should be those established during nebular condensation; in the latter, the original pattern should be modified by loss of the most mobile elements. These ten volatile/mobile elements in Karoonda are depleted relative to cosmic abundances by differing amounts (Table 1), in contrast to the situation in C1 and C2 chondrites. This fact alone does not distinguish between either alternative but those elements which are excessively depleted are instructive.

If Karoonda represents carbonaceous chondrite-like material metamorphosed in an open system, the order in which we list the elements should parallel the ease with which these elements are lost from the Karoonda precursor. We cannot be certain of the nature of this precursor or of its behavior on heating in the neighborhood of 450-600°C, a reasonable range for the hypothetical metamorphism of Karoonda. Nevertheless, all experiments on primitive chondrites demonstrate loss of Bi, In and Tl in this temperature range, with Tl losses exceeding those of Bi and In. Data for Murchison are typical of these trends,



Fig. 1. Depletion factors or atomic abundances of ten volatile/mobile trace elements and non-volatile Co relative to those in C1 chondrites. In addition to data for unheated Murchison (C2), Allende (C3) and Karoonda (C4) we include trends for Murchison heated at 500 and 600°C in a low-pressure environment. Elements most depleted in Karoonda are most mobile during heating at 400-600°C. Data for Murchison and Allende are consistent with the two-component mixing model, those for Karoonda suggest derivation by low-temperature, open-system metamor-

phism of C3 chondrite-like material.

and are illustrated in Fig. 1. [Cadmium is probably lost from Murchison even at 500°C and certainly at 600°C but its usual aberrant behavior (e.g. MATZA and LIPSCHUTZ, 1977) prompts us to omit it.] The trend of the Karoonda data matches this pattern. Furthermore, we note that the five elements, Se  $\rightarrow$  Te, which are depleted in Karoonda in proportions intermediate to those of Ga and In, Bi or Tl are 1-2  $\sigma$  lower in Murchison heated at 600°C than in unheated Murchison or samples heated at 500°C. (The uncertainty associated with Cs in Karoonda is unusually large, 12%, and it may well be less depleted, perhaps falling between Se and Ag.)

Data for the six volatile/mobile elements,  $Ga \rightarrow Te$ should delineate possible parent material. One may assume complete retention of all six elements or only of Ga and Se during metamorphism, in which case the respective mean depletion factors  $0.24 \pm 0.04$  or  $0.30 \pm 0.04$ , indicate the proportion of low-temperature material in the Karoonda precursor. In either case the data are consistent with a C3 progenitor, assuming the validity of the twocomponent model. In view of this last conclusion, it would have been best had we been able to compare trends for Karoonda with those in a heated *pristine* C3 chondrite rather than a C2 chondrite, Allende apparently having been mildly sintered (MCSWEEN, 1977b); we hope to perform such experiments in the future.

As mentioned, closed-system metamorphism should leave primary abundances unaltered and, if Karoonda experienced such an episode, its composition should reflect



Fig. 2. Comparison of empirical Bi, In and Tl data for Karoonda and heated Allende (numbers are  $100^{\circ}$ C temperature intervals) and Murchison with theoretical curves for condensation from a gas of cosmic composition at pressures of  $5 \times 10^{-5}$ ,  $10^{-4}$  and  $5 \times 10^{-4}$  atm (LARIMER, 1973). Data for Karoonda seem somewhat more consistent with simulated metamorphic trends than with theoretical condensation curves in the cases of Tl/Bi (a) and In/Tl (c); for In/Bi (b) no choice is possible.

nebular condensation effects. The pronounced slope of the depletion pattern for the ten volatile/mobile elements  $Ga \rightarrow Tl$  differs distinctly from the generally flat pattern for these elements in C1-3 chondrites (Fig. 1; cf. ANDERS

et al., 1976). Elements out of line in C3V chondrites include Ag, T1 and Cd; Cd is also exceptional in C30 chondrites. It is worthwhile considering these data in comparison with those in Karoonda to examine whether prior explanations can account for the Karoonda data.

In C3V chondrites the mean depletion factor for Ag --an element postulated by the two-component model to condense at 800 K--- is not as extreme as those for other volatile/mobile elements (postulated to condense at 700 to <480 K); this is attributed to a variation of the gas/dust ratio during condensation (cf. ANDERS et al., 1976). This situation is not observed in Karoonda. Silver is as depleted as Zn and more depleted than Se, yet both Se and Zn condense at <700 K according to the two-component model. The Tl abundance of Kaba is half that of Karoonda but Ag, Cd, Cs and In are definitely higher by factors of 2-3. ANDERS et al. (1976) attributed the low Tl content of Kaba to condensation of its parent material from a nebula unbuffered by Fe so that the H<sub>2</sub>S/He ratio would be but 0.75 of cosmic. The discrepancies between the four less mobile elements argue against this explanation for Karoonda. The excess Cd depletion in C30 chondrites can be accounted for by condensation from an Fe-buffered system (cf. ANDERS et al., 1976) but Cd is not excessively depleted in Karoonda relative to Bi or In. Thus the leads provided by data for other carbonaceous chondrites do not seem to predict the trend of the Karoonda data.

Finally we may compare trends for the hypothesized cosmothermometric elements Bi, In and Tl in Karoonda with those observed in heated Allende and Murchison (IKRAMUDDIN and LIPSCHUTZ, 1975; MATZA and LIPSCHUTZ, 1977) and predicted by the two-component model (e.g. LARIMER, 1973). When the data are normalized to Se or Ga as required by this model (cf. LARIMER, 1973), the Karoonda data seem to fit the Tl/Bi, In/Bi and In/Tl trends for heated Murchison quite well (Fig. 2). In the In/Bi case the fit to the condensation curves is also quite good; however the poorer fits in the other cases are not so serious as to indicate unambiguous disagreement (Fig. 2).

In our view the volatile/mobile element pattern in Karoonda seems quite consistent with that expected from open-system metamorphism of carbonaceous chondritelike, presumably pristine C3, material in a parent object at temperatures of 500-600°C. The agreement with trends expected for closed-system metamorphism seems less good and it may be possible to reconcile the Karoonda data with those expected from the condensation model. Coolidge, being less-severely metamorphosed, should be closer in composition to its parent material. Indeed we would have preferred dealing with a more severely metamorphosed carbonaceous chondrite than Karoonda in order to permit an unambiguous choice between the metamorphic models. We can only hope that one such meteorite will arrive in the future.

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#### REFERENCES

ANDERS E., HIGUCHI H., GANAPATHY R. and MORGAN J. W. (1967) Chemical fractionations in meteorites--IX. C3 chondrites. *Geochim. Cosmochim. Acta* 40, 1131-1139.

BINZ C. M., IKRAMUDDIN M., REY P. and LIPSCHUTZ M. E. (1976) Trace elements in primitive meteorites—VI. Abundance patterns of thirteen trace elements and interelement relationships in unequilibrated ordinary chondrites. *Geochim. Cosmochim. Acta* **40**, 59-71.

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- BINZ C. M., KURIMOTO R. K. and LIPSCHUTZ M. E. (1974) Trace elements in primitive ineteorites—V. Abundance patterns of thirteen trace elements and interelement relationships in enstatite chondrites. Geochim. Cosmochim. Acta 38, 1579 1406.
- CLAYTON R. N., ONUMA N., GROSSMAN L. and MAYEDA T. K. (1977) Distribution of the pre-solar component in Allende and other carbonaceous chondrites. Earth Planet. Sci. Lett. 34, 209-224.
- IKRAMUDDIN M., BINZ C. M. and LIPSCHUTZ M. E. (1976) Thermal metamorphism of primitive meteorites—II. Ten trace elements in Abee enstatite chondrite heated at 400-1000°C. Geochim. Cosmochim. Acta 40, 133-142.
- IKRAMUDDIN M. and LIPSCHUTZ M. E. (1975) Thermal metamorphism of primitive meteorites—I. Variation of six trace elements in Allende carbonaceous chondrite heated at 400-1000°C. Geochim. Cosmochim. Acta 39, 363-375.
- IKRAMUDDIN M., MATZA S. D. and LIPSCHUTZ M. E. (1977) Thermal metamorphism of primitive meteorites—V. Ten trace elements in Tieschitz H3 chondrite heated at 400-1000°C. Geochim. Cosmochim. Acta, 41, 1247-1256.
- LARIMER J. W. (1973) Chemical fractionations in meteor-

ites-VII. Cosmothermometry and cosmobarometry. Geochim. Cosmochim. Acta 37, 1603-1623.

- MATZA S. D. and LIPSCHUTZ M. E. (1977) Thermal metamorphism of primitive meteorites—VI. Eleven trace elements in Murchison C2 chondrite heated at 400-1000°C, Proc. Eighth Lunar Sci. Conf. To be published.
- McSween H. Y. Jr. (1977a) Carbonaceous chondrites of the Ornans type: a metamorphic sequence. Geochim. Cosmochim. Acta 41, 477-491.
- MCSWEEN H. Y. JR. (1977b) Petrographic variations among carbonaceous chondrites of the Vigarano type. Geochim. Cosmochim. Acta, submitted.
- VAN SCHMUS W. R. (1969) Mineralogy. petrology. and classification of types 3 and 4 carbonaceous chondrites. *Meteorite Research* (editor P. M. Millman) pp. 480-491.
- VAN SCHMUS W. R. and HAYES J. M. (1974) Chemical and petrographic correlations among carbonaceous chondrites. *Geochim. Cosmochim. Acta* 38, 47–64.
- VAN SCHMUS W. R. and WOOD J. A. (1967) A chemicalpetrologic classification for the chondritic meteorites. *Geochim. Cosmochim. Acta* 31, 747-765.
- WIIK H. B. (1969) On regular discontinuities in the composition of meteorites. Commentat. Phys. Math. 34, 135-145.