

THE THERMODYNAMIC PROPERTIES AND ORIGIN OF OSBORNITE, SINOITE, CARLSBERGITE AND DAUBREELITE IN METEORITES: I. L. Khodakovsky, M. I. Petaev, Vernadsky Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences, Moscow, USSR

The consideration of stability of osbornite,  $TiN$ , carlsbergite,  $CrN$ , sinoite,  $Si_2N_2O$  and daubreelite,  $FeCr_2S_4$ , in the Fe-Cr-Ti-Si-O-N-S system is of great interest in solving of many problems on meteorite origin. Despite these minerals are rarely occurred in meteorites the former are considered as the indicators of meteoritic origin parameters such as temperature, pressure and oxygen, nitrogen and sulfur fugacity.

On the base of mineralogical data review it was shown [1] that the sinoite and osbornite are typomorphic minerals of enstatite chondrites. So sinoite is found only in the type II chondrites (in 6 from 9 known meteorites), osbornite - in the type II chondrites and aubrites. The type I chondrites with high silicon content in metal phase don't contain nitrides except the sole occurrence in Abee [2]. The carlsbergite has been identified in more than 70 meteorites, mostly members of Ga-Ge group IIIA, but it is also found in groups I and IIA [3]. The daubreelite is an ordinary accessory mineral both in the enstatite and in iron meteorites, but it was not found on the Earth. Structural relations between daubreelite and other minerals are of great interest. It is usually found in assemblage with the troilite as lamellae parallel (001) of troilite. Ramdohr [2] supposed that these structures are to be considered as the evidence of daubreelite formation under exsolution in the  $FeS-FeCr_2S_4$  system. The euhedral daubreelite crystals are described only in meteorites where the troilite is absent. It is noted [2] that the transformation  $FeCr_2S_4$  into  $FeCr_2O_4$  is not observed, but in Pes'yanoe aubrite the daubreelite substitutes for chromite. In the enstatite chondrites Ramdohr observed also the daubreelite assemblage with hexagonal or pseudohexagonal chromium sulfide with Cr/S ratio about 2:3. In this assemblage the daubreelite has a behavior similar to the hexagonal modification. We note that the daubreelite is transformed into hexagonal  $FeCr_2S_4$  with NiAs type structure at  $\sim 1335K$  [4, 5]. Such structural relations of daubreelite with other minerals are considered as the probable result of the alteration processes of the primordial meteoritic matter after the condensation.

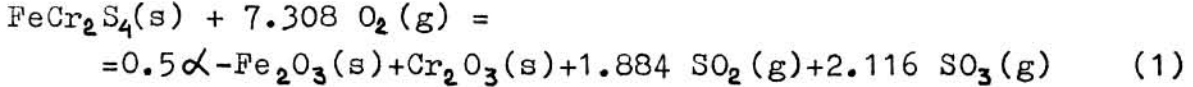
The interpretation of the mineral assemblages in question is carried out in terms of thermodynamics. It is necessary not only to evaluate the possibility of osbornite, sinoite, carlsbergite and daubreelite formation during the nebula condensation, but to characterize the probable alteration processes during the primordial meteoritic matter evolution.

Unfortunately the necessary thermodynamical data on certain compounds involved in the considered system is either unavailable or contradictory. Elsewhere [1] we reviewed all available experimental data and recommended the most reliable values of thermodynamical properties of Ti, Cr and Si nitrides. In addition we measured the specific heat of daubreelite in the 58 - 300K temperature range. These data along with the data on specific heat in the 1 - 30K [6] and 173 - 673K [7] temperature ranges permitted to obtain the standard entropy and the temperature dependence of

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heat capacity (Table 1). The value of  $\Delta H_f^\circ(298.15 \text{ K}, \text{FeCr}_2\text{S}_4) = -107.8 \pm 1.9 \text{ kcal/mol}$  was calculated from the data of enthalpy oxidation reaction measurement of  $\text{FeCr}_2\text{S}_4$  by air at 975K



provided  $\Delta H_{\text{exp}} = -536.16 \pm 1.7 \text{ kcal/mol}$  and thermodynamic properties of other compounds from [9]. Tretyakov et al. [10] estimated the  $H_f^\circ(298.15\text{K}, \text{Cr}_2\text{S}_3)$  value as  $-81.5 \pm 1.5 \text{ kcal/mol}$ . The temperature dependence of heat capacity was obtained from the high-temperature enthalpy measurements of  $\text{Cr}_2\text{S}_{2.98}$  in the 400 - 1700K temperature range [11]. The entropy was estimated by Latimer's method (Table 1).

For the oxygen and nitrogen fugacity estimation in equilibrium with the minerals of enstatite and iron meteorites the stabilities of the osbornite, sinoite, carlsbergite and daubreelite in respective systems at 800°C were evaluated. This temperature corresponds to equilibrium Fe, Si and Ca partition between minerals of enstatite chondrites [12]. In our calculations the activities of solids are assumed to be unit except Si. The activity of Si determined by equation:  $a_{\text{Si}} = \gamma_{\text{Si}}[\text{Si}]$ . The value of  $\lg a_{\text{Si}} = -5.1$

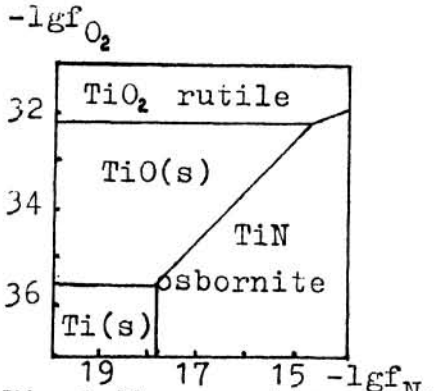


Fig.1. Phase relations in the Ti-N-O system at 800°C.

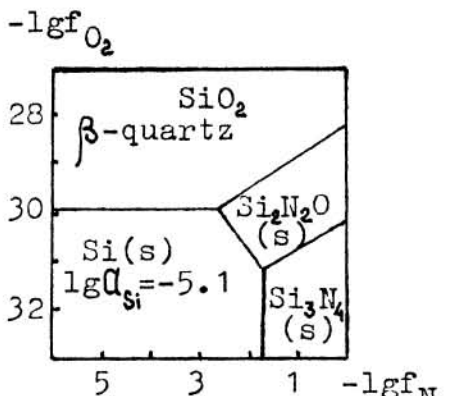


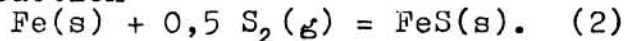
Fig.2. Phase relations in the Cr-N-O system at 800°C.

corresponds to the  $\lg \gamma_{\text{Si}} = -3.5 \pm 0.5$  and the average Si content in the metal phase of type II enstatite chondrites is found to be ca 2.6 mol%.

The results obtained are presented at the Fig.1-3. Sinoite,  $\text{Si}_2\text{N}_2\text{O}$ , unlike osbornite, TiN, is stable within narrow interval of oxygen and nitrogen fugacity values providing its occurrence in the type II chondrites only.

The carlsbergite is stable in the Cr-N-O system (Fig.3) at relatively high nitrogen fugacity. This fact implies that the iron meteorites containing carlsbergite, CrN, as well as enstatite chondrites were presumably formed at similar physico-chemical conditions.

At the Fig.4 the stability diagram of daubreelite in the Fe-Cr-S-O system is plotted. The sulfur fugacity is calculated from Fe-FeS buffer reaction



The thermodynamical properties of  $\text{Fe}(\text{s})$ ,  $\text{FeS}(\text{s})$  and  $\text{S}_2(\text{g})$  are taken from [9].

As shown at Fig.4 the daubreelite will dissociate at  $T = 595 \pm 125 \text{ K}$  according to the reaction

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TABLE 1.

Compound	$-\Delta H_f^\circ(298)$ kcal/mol	$S^\circ(298)$ cal/mol·K	$C_p^\circ = a + b \cdot 10^{-3} T - c \cdot 10^{-5} T^2$			Temperature range (K)
			a	b	c	
TiN osbornite	80.7±0.3	7.25±0.04	11.91	0.94	2.96	298 - 1738
Cr <sub>2</sub> N (s)	31.5±0.6	15.3±0.4	15.05	6.58	-	298 - 1400
CrN carlsbergite	28.2±0.4	8.8±0.4	11.10	1.58	-	298 - 1800
Si <sub>3</sub> N <sub>4</sub> (s)	188.3±0.6	15.79±0.15	19.55	19.80	1.58	298 - 1132
Si <sub>2</sub> N <sub>2</sub> O sinoite	210.3±3.7	10.84±0.11	13.91	11.22	0.79	298 - 1132
FeCr <sub>2</sub> S <sub>4</sub> daubreelite	107.8±1.9	49.2±0.6	54.04	-47.07	2.15	298 - 1335
Cr <sub>2</sub> S <sub>3</sub> (s)	81.5±1.5*	36.0*	29.11	5.72	-	298 - 1700

\* Estimated value

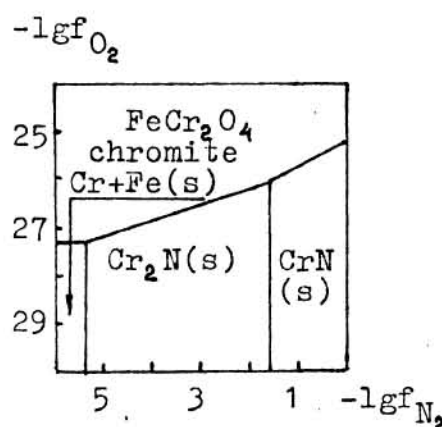


Fig. 3. Phase relations in the Fe-Cr-N-O system at 800°C.

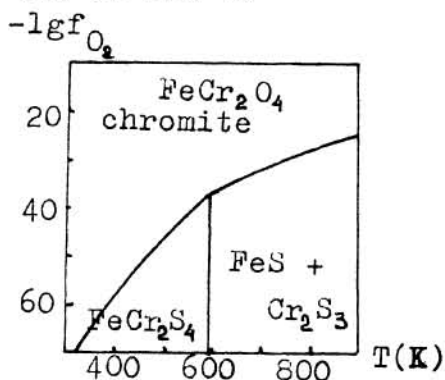
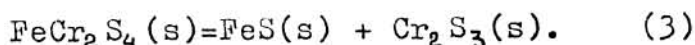


Fig. 4. Phase relations in the Fe-Cr-S-O system.



Whereas under experimental conditions [4, 5]  $\text{FeCr}_2\text{S}_4$  did not dissociate at much higher temperatures. The reason of this discrepancy might be explained by the slow rate of daubreelite dissociation. The mineralogical data [2] support the assumption of the reality of the reaction (3) during the meteoritic matter evolution.

Thus we suggest two alternative conclusions: (a) the metastable daubreelite being the high-temperature condensate (hexagonal at  $T > 1335\text{K}$ ) was dissociated in the conditions of very slow cooling; (b) the early formed daubreelite was slowly heated up to the temperature higher than  $595^{+125}_{-140}\text{K}$ .

References: (1) Khodakovsky I. L., Petaev M. (1981), *Geokhimiya*, 3, in press; (2) Ramdohr (1973), *The Opaque Minerals in Stony Meteorites*, *Elv. Publ. Co.*; (3) Buchwald V. F., Scott E. R. D. (1971), *Nat. Phys. Sci.*, 233, 113; (4) Albers W. et al. (1965), *Sol. State Com.*, 3, 417; (5) Rooymans C. J. M. (1967), *Col. Gen. Nat. Rech. Sci.*, N157, 63; (6) Lotgering F. K. et al. (1975), *Sol. State Com.*, 17, 1149; (7) Shchelkotunov V. A. et al. (1977), *Izv. AN SSSR, Neorg. Mater.*, 13, 1716; (8) Kessler J. et al. (1976), *J. Chem. Ther.*, 8, 101; (9) Naumov G. B. et al. (1974), *Handbook Thermod. Data*; (10) Tretyakov Y. D. et al. (1977), *J. Sol. State Chem.*, 20, 345; (11) Volovic L. S. et al. (1977) *Abs. VII Vses. Conf. Calor.*, Czernogolovka, 349; (12) Larimer J. W., Buseck P. R. (1974), *GCA*, 38, 471.