

Chaoite Formation from Carbon-Bearing Fluid at Low *PT* Parameters

S. K. Simakov¹, A. E. Kalmykov², L. M. Sorokin², M. P. Novikov³, I. A. Drozdova⁴,
M. A. Yagovkina², and E. A. Grebenshchikova²

Presented by Academician A. A. Marakushev April 16, 2004

Received May 17, 2004

At present, chaoite is a less studied member among the known crystalline carbon phases. The X-ray identify of chaoite to known carbyne species, as well as its physicochemical and mechanical properties, shows that this phase belongs to the carbyne–diamond group [1]. The first finding of chaoite in association with graphite was first reported from the Ries impact crater [5]. An analogous carbon phase was found in diamond–graphite intergrowths in the Urei meteorite [1]. Later, chaoite was synthesized at high temperatures by direct heating under vacuum [6] and at high dynamic pressures [3] from highly crystalline graphite. The above data apparently suggest that chaoite is a high-temperature phase that can occur in nature only under superhigh temperatures, which correspond to meteorite structures and lower mantle. However, this is inconsistent with the presence of impurities of carbyne (a high-temperature carbon phase genetically related to chaoite) in natural graphites [7].

We studied the formation of free carbon from carbon-bearing gases at 500°C and total pressure of 1000 atm. The carbon-bearing gases were obtained from alcohol with the addition of organic nitrogen-bearing compounds. Experiments were conducted in titanium autoclaves (BT-8 alloy) at the Institute of Experimental Mineralogy, Chernogolovka. Metallic iron served as an oxygen buffer. The run duration was 5–7 days. After treatment in concentrated HCl to remove possible

metallic phases and iron oxides, experimental products were studied by the X-ray diffraction method on a D/max-RC diffractometer (Rigaku, Japan). Reflections were obtained with $\text{CuK}\alpha$ radiation ($2\theta = 0^\circ\text{--}100^\circ$, step

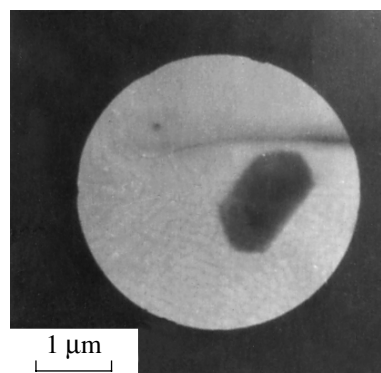


Fig. 1. Chaoite particle.

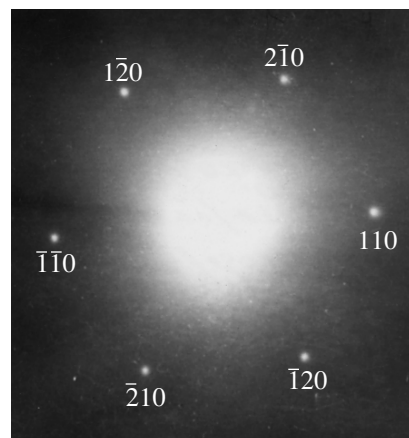


Fig. 2. Microdiffraction pattern of the chaoite particle. Measured $d_{110} = 4.48 \text{ \AA}$ (4.47 Å, according to the ASTM database).

¹ St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199164 Russia;
e-mail: simakov@ap1250.spb.edu

² Ioffe Physico-Technical Institute, Russian Academy of Sciences, ul. Politekhnikeskaya 26, Moscow, 194021 Russia

³ Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

⁴ Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, nab. Makarova 2, St. Petersburg, 199034 Russia

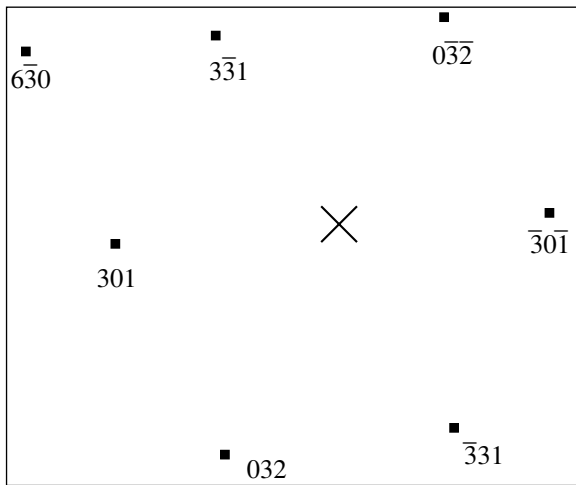


Fig. 3. Microdiffraction pattern of the same particle tilted at 20°. Deterioration of the quality of microdiffraction image as compared to that in Fig. 2 is related to the increase of efficient thickness of the sample at tilting.

0.01°, and scan rate 1°/min). Using this method, we identified nanographite. After this, the products were treated in concentrated HClO₄ to remove graphite. The

Table 1. Comparison of interplanar spacings based on the microdiffraction pattern in Fig. 3 with data on chaoite presented in the ASTM database (card 22-1069)

<i>hkl</i>	Chaoite (ASTM), Å	<i>d</i> _{exp} , Å
301	2.55	2.58
331	2.55	2.54
032	2.425*	2.4
630	1.49*	1.51

* Interplanar spacings calculated from the chaoite lattice parameters (*a* = 8.948 Å, *c* = 17.078 Å)

Table 2. Comparison of angles between reflecting planes based on the microdiffraction pattern in Fig. 3 with values calculated from the reflection indices recorded in the microdiffraction pattern

Planes		Calculated degrees	Experimental degrees
<i>H</i> ₁ <i>k</i> ₁ <i>l</i> ₁	<i>H</i> ₂ <i>k</i> ₂ <i>l</i> ₂		
301	331	63	64
331	630	32	33
301	032	58	59
301	331	116	116

powder that remained after washing was loaded in colloid solution in amyl acetate and then applied on the water surface. The film obtained was transferred onto a grid for electron microscopic investigation.

Samples were studied with an EM-200 electron microscope at an accelerating voltage of 100 kV. The carrier film universally contains particles with hexagonal edges (Fig. 1). Their microdiffraction patterns have a sixfold axis of symmetry (Fig. 2), which corresponds to a hexagonal or cubic lattice. Interplanar spacings determined from Fig. 2 within error limits coincide with those for hexagonal chaoite (*a* = 8.948 Å, *c* = 14.078 Å) presented in the ASTM database (card 22-1069). None of the known cubic carbon forms show such interplanar spacings. The specimen was tilted at 20° to ascertain that the particles observed represented crystalline chaoite. The microdiffraction pattern obtained (Fig. 3) cannot be indexed as a cubic lattice. However, recorded reflections that fit the regular lattice (Tables 1, 2) correspond to those expected from the planes with zone axis (123). Reflections not fitting the regular lattice were presumably produced by some other crystalline particle, which was not in the reflective position prior to specimen tilting. The presence of reflections (Fig. 3) that are absent in the ASTM database can be explained by secondary electron diffraction.

Thus, the results indicate that chaoite can be formed from carbon-bearing fluids under low temperatures and pressures.

REFERENCES

1. G. P. Vdovykin, *Geokhimiya*, No. 9, 1145 (1969).
2. V. M. Mel'nichenko, Yu. N. Nikulin, and A. M. Sladkov, *Dokl. Akad. Nauk SSSR* **267**, 1150 (1982).
3. V. V. Sobolev, R. P. Didyk, V. Ya. Slobodskoi, *et al.*, *Cutting Instrument: Diamonds* (NIIMash, Moscow, 1984), Issue 1, pp. 5–6 [in Russian].
4. V. V. Sobolev, V. Ya. Slobodskoi, S. N. Selyukov, *et al.*, *Zap. Vses. Mineral. O-va* **115**, 218 (1986).
5. A. Gorsev and G. Donney, *Science* **161**, 363 (1968).
6. A. G. Whittaker and W. Hills, U.S. Patent No. 3 733 394 (1970).
7. A. G. Whittaker, *Carbon* **17**, 21 (1979).