Silicon Oxynitride: A Meteoritic Mineral

Abstract. *Silicon oxynitride, a new mineral, has been discovered in the Jajh deh Kot Lalu enstatite chondrite. Nitrogen and oxygen have been measured quantitatively with an electron microprobe by means of prototypes of newly developed curved crystal detection systems. X-ray diffraction patterns were obtained from silicon oxynitride separated from the meteorite and from synthetic* Si_2N_2O.

The Jajh deh Kot Lalu meteorite fell at the village of the same name (lat. 26°45′N; long. 68°25′E) in the Sind province of Pakistan on 2 May 1926. The circumstances of the fall and the megascopic and microscopic features of the meteorite were briefly described by Hobson (*1*). Recent examination of a specimen (No. 3954) of this meteorite in the collection of the American Museum of Natural History showed that it belongs to the small group of enstatite chondrites, a group that is remarkable for a high degree of reduction and the presence of unusual minerals. On this account a detailed investigation of its mineralogical and chemical composition was carried out (*2*).

Fig. 1. Several grains of the silicon oxynitride (light gray, center of the picture and right and left sides), enstatite (dark gray matrix), and metallic nickel-iron (white). Reflected light.

The meteorite consists largely (50 to 60 percent) of enstatite and nickel-iron (about 20 percent). Minor amounts of plagioclase (about 10 percent) and troilite (about 5 percent) are present. Accessory minerals include pigeonite, daubreelite, oldhamite, ferroalabandite, graphite, tridymite, and the new mineral, silicon oxynitride, which was recognized by electron microprobe analysis (*2*).

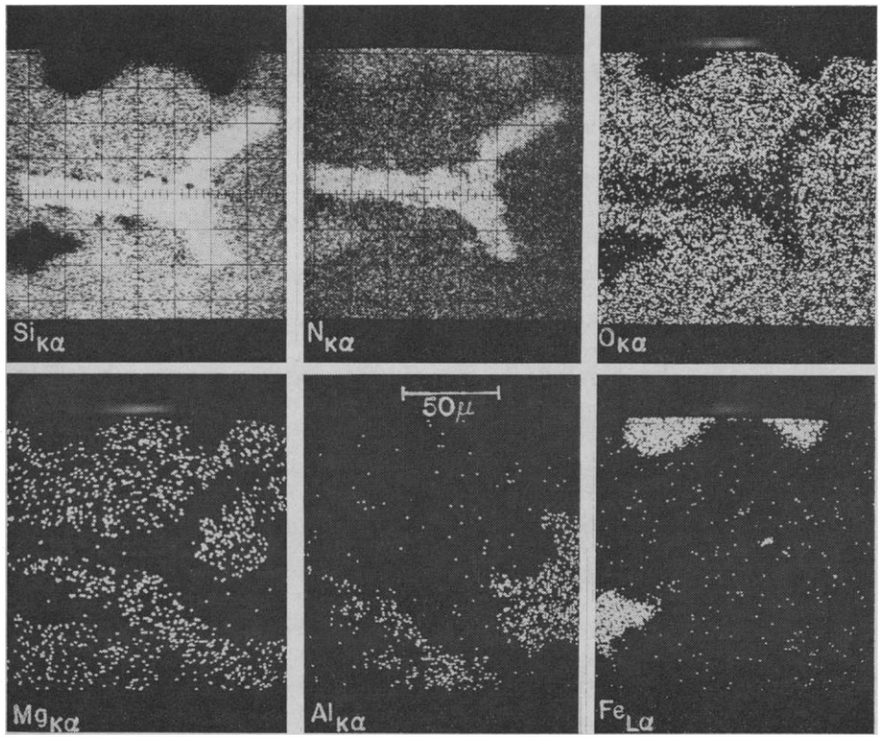

Fig. 2. Semiquantitative electron-beam scanning pictures of the silicon oxynitride (high silicon and nitrogen intensities). Matrix is enstatite (high Mg) with some plagioclase (high Al) and metallic nickel-iron grains (high Fe); 5 kev accelerating potential.

At about the same time, synthetic Si_2N_2O (*3*) was prepared by heating a mixture of silicon and quartz powder in an atmosphere of nitrogen at 1450°C. The substance is orthorhombic, with cell dimensions of $a = 8.843$ Å, $b = 5.473$ Å, and $c = 4.835$ Å; there are four formula units in the unit cell. The calculated density is 2.84. At our request, Brosset and Idrestedt kindly sent us a sample of their synthetic material for comparison with our meteoritic mineral. The sample is a fine-grained white powder.

The mineral in the meteorite can be distinguished in a thin section by its high birefringence; whereas all the other transparent minerals show first-order gray or white interference colors, the new mineral shows bright higher-order colors. It occurs as irregular grains or occasional lath-like crystals up to 0.2 mm long, the individual grains frequently being aggregated into larger patches. It is colorless in thin sections and its refractive index is higher than that of the surrounding enstatite. In polished sections it appears light gray, and it is distinctly different from the surrounding enstatite (Fig. 1).

The chemical composition was determined in polished sections of the meteorite by electron microprobe techniques (*2*). During analysis, the exact position of the impingement of the electron beam on the mineral was observed as a distinctive greenish-yellow fluorescence. The mineral was qualitatively analyzed for elements of atomic numbers, $Z = 5$ through 92 (boron through uranium). Only the elements Si, N, and O were detectable (Table 1). Electron-beam scanning pictures were taken in order to illustrate semiquantitatively the composition of the mineral and its surroundings (Fig. 2). Quantitative analyses of the mineral were carried out by moving the mineral grains in 3-μ steps under a stationary electron beam, thus covering the mineral with rows of point integrations (Fig. 3). Nitrogen and oxygen were measured by dispersive detection systems recently developed at the Hasler Research Center, Applied Research Laboratories. Nitrogen ($N_{K\alpha}$) was measured with a barium stearate monolayer pseudocrystal spectrometer, while oxygen ($O_{K\alpha}$) was determined with a

Table 1. Composition of silicon oxynitride from the Jajh deh Kot Lalu enstatite chondrite as obtained by electron microprobe techniques, in comparison to theoretical Si_2N_2O (weight percent).

Element	Silicon oxynitride from Jajh deh Kot Lalu*	Si_2N_2O theoretical composition
Si	56.6	56.1
N	31.5	27.9
O	13.1	15.9
Total	101.2	99.9

* Corrected characteristic x-ray intensity ratios. Accelerating potential was 5 kev. Mass absorption corrected by using experimental $f(\chi)$ curves for $C_{K\alpha}$ and $Al_{K\alpha}$ given by Green (*4*) and mass absorption coefficients given by Henke *et al.* (*5*). Secondary fluorescence was insignificant according to Wittry's (*6*) formulas. Atomic number effect corrections for Si and O were derived from measurements made on quartz as compared to enstatite. Enstatite and BN were used as standards. Accuracy of the Si values is about 2 percent and of the O and N values probably not better than 15 percent.

Table 2. X-ray powder diffraction data for synthetic Si_2N_2O and for the fraction of density 2.80 to 2.85 from the Jajh deh Kot Lalu enstatite chondrite. Conditions: $Cu_{K\alpha}$ radiation, Ni filter, camera diameter 114.6 mm. Visual estimation of intensities was normalized to the most intensive lines; $d = 4.43$ for synthetic Si_2N_2O and $d = 3.19$ for Jajh deh Kot Lalu. *e*, Enstatite. *p*, Plagioclase. *s*, Si_2N_2O.

Synthetic Si_2N_2O		Jajh deh Kot Lalu	
d	*I*	*d*	*I*
		6.42 (p)	5
4.66	8	4.65 (s)	4
4.43	10	4.44 (s)	5
4.13	3		
		4.04 (p)	7
		3.74 (p)	5
3.72	1		
		3.65 (p)	2
3.36	10	3.36 (s)	6
		3.19 (p, e)	10
		2.94 (p)	4
		2.87 (p, e)	4
2.74	2		
		2.71 (e)	1
		2.66 (p)	1
2.61	5	2.60 (s)	1
		2.53 (e)	6
		2.48 (e)	4
2.42	5	2.43 (s)	1
2.39	4	2.38 (s)	2
2.30	3	2.30 (s)	2
2.22	1		
2.16	1	2.17 (s)	2
2.10	1		
		2.06 (e)	1
		1.99 (e)	1
		1.97 (e)	1
1.82	1	1.83 (p)	2
1.79	1	1.79 (p)	1
1.77	1	1.77 (e)	3
1.69	2		
1.62	1	1.61 (e)	2
1.60	2		
1.56	2		
1.53	1		
1.48	1	1.49 (e)	5
1.44	1		
1.39	2	1.39 (s, e)	2
1.37	2		
1.33	1	1.33 (s)	2
1.31	2		
1.28	1	1.27 (s, e)	2
1.26	2		

potassium acid phthalate crystal spectrometer. A flow detector with an ultrathin nitrocellulose window was used for both $N_{K\alpha}$ and $O_{K\alpha}$. The quantitative data were corrected for detector deadtime, background, mass absorption, secondary fluorescence, and atomic number. There was no measurable wavelength shift between the mineral and the standards.

The average composition of the mineral obtained from several hundred measurements is given in Table 1 in comparison to theoretical Si_2N_2O. The composition of the mineral is rather homogeneous and variations from the average are usually within the precision of the method (2σ values in Fig. 3). Minor fluctuations, particularly in the case of nitrogen and oxygen, may be due in part to surface irregularities, which possibly influence the soft radiations considerably. In some instances a decrease of Si and N goes parallel with an increase of oxygen (Fig. 3). This phase has not yet been identified. Figure 3 also shows a slight increase of oxygen and decrease of nitrogen towards the grain boundaries of the mineral. Table 1 indicates that the new mineral may be slightly richer in nitrogen and poorer in oxygen than the synthetic Si_2N_2O.

In order to separate the mineral for further studies, a 5-gram sample of the meteorite was carefully crushed and fractionated in mixtures of methylene iodide and acetone of different densities. The new mineral was concentrated in the fraction whose density was 2.80 to 2.85, which indicated that its density was close to that calculated for Si_2N_2O. Refractive indices of individual grains (measured by the immersion method) are $\alpha = 1.740$, $\gamma = 1.855$. A suitably oriented grain for determination of β was not observed; however, β appears to be close to γ, implying that the mineral is optically negative, with a small axial angle. The crystals are length-slow, that is, $\gamma = c$. The synthetic material is too fine-grained to measure the refractive indices; it is markedly birefringent, with a mean refractive index about 1.79.

The *d*-spacings from an x-ray powder photograph of synthetic Si_2N_2O and those for the 2.80 to 2.85 density fraction of the meteorite are given in Table 2. This fraction contains only a minor amount of the new mineral mixed with a larger amount of locked

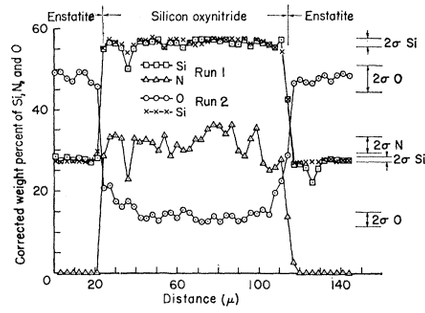

Fig. 3. Quantitative Si, Ni, and O electron microprobe analyses of the silicon oxynitride grain shown in Fig. 2. Quantitative analyses were performed by traversing the grains with point by point integrations 3 microns apart.

grains of enstatite and plagioclase; nevertheless, the powder photograph shows all the major lines of Si_2N_2O. Slight intensity differences are presently unexplained.

The presence of this mineral in a meteorite is extremely interesting in terms of origin, since it implies the availability of nitrogen in the environment in which the meteorite crystallized.

We propose the name *sinoite*, which is derived directly from the chemical formula, for this new mineral.

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References and Notes

1. G. V. Hobson, *Rec. Geol. Surv. India* **60**, 150 (1927).
2. K. Keil and C. A. Andersen, *Trans. Am. Geophys. Union* **45**, 86 (1964); *Geochim. Cosmochim. Acta*, in preparation.
3. C. Brosset and I. Idrestedt, *Nature* **201**, 1211 (1964).
4. M. Green, *International Symposium X-ray Optics and X-ray Microanalysis, 3rd, Stanford University, 1962*, H. H. Pettee, V. E. Cosslett, A. Engström, Eds. (Academic Press, New York, 1963), pp. 361–377.
5. B. L. Henke, R. White, B. Lundberg, *J. Appl. Phys.* **28**, 98 (1957).
6. D. B. Wittry, *Univ. S. Calif. Tech. Rept. No. 84–204* (1962).

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