

was iso-chemical, these compositions would indicate temperatures of formation of 510°–515° C. Because natural monoclinic pyrrhotite shows little departure from the composition, $\text{Fe}_{0.875}\text{S}$, however, the close coincidence of the crystallization temperatures deduced from the compositions of the co-existing hexagonal and monoclinic pyrrhotites may be fortuitous². In other sulphide deposits, low-temperature re-equilibration of hexagonal pyrrhotite has resulted in the formation of monoclinic and monoclinic + hexagonal-pyrrhotite, and hexagonal pyrrhotite having a composition in the approximate range $\text{Fe}_{0.895-0.899}\text{S}$. Intermediate pyrrhotite ($\text{Fe}_{0.912}\text{S}$) and, especially, troilite may be subordinate or absent in such assemblages (unpublished work).

Table 1. X-RAY DATA FOR PYRRHOTITES FROM THE GREAT SULPHUR VEIN

Locality ¹⁰	Assemblage	Monoclinic pyrrhotite		Inter- mediate hexagonal pyrrhotite	Troilite
		$d(202)$ (Å)	$d(202)$ (Å)	$d(102)$ (Å)	$d(102)$ (Å)
Aglionby Beck	Quartz, pyrrhotite, pyrite	2.0641	2.0525		
Cross Gill	Quartz, pyrrhotite, pyrite, sphalerite	2.0636	2.0530	2.0707	2.0932
St. John's Mine	Quartz, pyrrhotite, pyrite	2.0635	2.0514	2.0700	2.0936
St. John's Mine	Quartz, pyrrhotite, sphalerite, chalcocopyrite	2.0621	2.0522	2.0703	
St. John's Mine	Quartz, pyrrhotite, pyrite	2.0630	2.0538	2.0703	

It should also be emphasized that pyrrhotite occurring, with or without associated pyrite, in low- to high-grade regionally metamorphosed rocks and in unmetamorphosed sediments is generally monoclinic and very iron-deficient. This feature prevents the estimation of the maximum temperatures of metamorphism on the basis of pyrrhotite compositions (unpublished work).

Examination of several pyrrhotite-bearing specimens from the Great Sulphur Vein¹⁰ has shown that, as found by Sawkins *et al.*¹, monoclinic pyrrhotite predominates over hexagonal, which is represented only by troilite and intermediate pyrrhotite (Table 1). The hexagonal phases have compositions identical to those observed in the Ylöjärvi deposit and at other localities. The ease with which they could be magnetically separated from each other suggests that the troilite and intermediate pyrrhotite occur as granular, rather than fine lamellar, intergrowths.

These few data are in fairly good agreement with those given by Sawkins *et al.*¹, and generally support the low-temperature origin of the vein assemblages. Hexagonal pyrrhotite with a (102) spacing of 2.088 Å was not, however, detected by me. There are apparently no reliable records of homogeneous natural pyrrhotites having compositions between those of troilite and intermediate pyrrhotite ($\text{Fe}_{0.912}\text{S}$), perhaps reflecting the presence of a solvus between these compositions at temperatures below c. 200° C (von Gehlen; personal communication). Cooling of iron-rich pyrrhotites from moderate temperatures (> 250° C) probably invariably results in the mutual exsolution of troilite and intermediate pyrrhotite, but primary crystallization at low temperatures might permit the formation of, presumably, metastable pyrrhotites within the proposed two-phase region.

A. H. CLARK

Department of Geological Sciences,
McGill University, Montreal, Canada.

¹ Sawkins, F. J., Dunham, A. C., and Hirst, D. M., *Nature*, **204**, 175 (1964).

² Arnold, R. G., *Econ. Geol.*, **57**, 72 (1962).

³ Grenvold, F., and Haraldsen, H., *Acta Chem. Scand.*, **6**, 1452 (1952).

⁴ Gehlen, K. von, Ann. Rept. Director Geophys. Lab., Carnegie Inst., Washington, *Year Book 62*, 213 (1963).

⁵ Clark, A. H., unpubl. Ph.D. thesis, Univ. Manchester (1964).

⁶ Clark, A. H., *Geologi*, **10**, 145 (1964).

⁷ Byström, A., *Arkiv Kemi, Mineral., Geol.*, **19** B, No. 8 (1945).

⁸ Evans, H. T., Milton, C., Chao, E. C. T., Adler, I., Mead, C., Ingram, B., and Berner, R. A., *U.S. Geol. Surv. Prof. Paper*, 475-D, D64 (1964).

⁹ Kullerud, G., Doe, B. R., Buseck, P. R., and Tröfthen, P. F., Ann. Rept. Director Geophys. Lab., Carnegie Inst., Washington, *Year Book 62*, 210 (1963).

¹⁰ Dunham, K. C., *Mem. Geol. Surv. Great Britain (H.M.S.O.)*, 1948.

WE welcome the preceding communication by Dr. A. H. Clark, which does much to clarify the problem of low-temperature pyrrhotites. We wish to point out that our only intention was to question the use of experimentally inverted monoclinic pyrrhotite as a geological thermometer (Buseck¹, Kullerud *et al.*²) and to show that in some natural occurrences the use of inverted monoclinic pyrrhotite produced results at variance with independent temperature data obtained from fluid inclusions.

F. J. SAWKINS
A. C. DUNHAM
D. M. HIRST

Department of Geology,
University of Durham.

¹ Buseck, P. R., Annual Report of the Director of the Geophysical Laboratory, Carnegie Institution, Washington, *Year Book 61*, 161 (1962).

² Kullerud, G., Doe, B. R., Buseck, P. R., and Tröfthen, P. F., Ann. Rept. Director Geophys. Lab., Carnegie Inst., Washington, *Year Book 62*, 210 (1963).

GEOCHEMISTRY

Fixation of Nitrogen by Aurora and its Contribution to the Nitrogen Balance of the Earth

CONSIDERABLE amounts of energy are dissipated in the upper atmosphere of the Earth by such geophysical phenomena as aurora, air glow and particulate bombardment. It is generally believed¹ that the dissipation of this energy leads to the formation of chemical species among which are oxides of nitrogen or their corresponding charge species. If these chemical species could reach the surface of the Earth they would contribute nitrate and nitrite to the biosphere. One of the aims of the Eighth Victoria University Antarctic Expedition was to estimate the magnitude of this effect by the chemical analysis of snow at the South Pole.

The South Pole was chosen because (a) thunderstorms, the usually accepted source of NO_2' and NO_3' in the atmosphere, are unknown; (b) if snow is collected from depths corresponding to times before human activities at the Pole, the chances of biological contamination are diminishingly small. The South Pole, being situated at 9,300 ft. on an ice plateau, is so remote that all normal sources of possible contamination can be eliminated; (c) the South Pole is surrounded by the auroral zone.

Freshly fallen snow (November 3, 1963) and snow from the year 1962–63 was collected one mile from South Pole Station. Samples of snow from 3 ft. inside the wall of the snow mine 44 ft. below the surface (approximately 100 years old) were analysed at the Base for $\text{NO}_3' + \text{NO}_2'$ using the phenoldisulphonic acid method as described in ref. 2, except that a 500-ml. sample was used. All samples measured contained 0.005 p.p.m. N as $\text{NO}_3' + \text{NO}_2'$.

The nitrate plus nitrite content of South Polar snow was almost equal to that of the chloride content (0.027 p.p.m.). This is in marked contrast to analysis of snow from other areas less remote from the oceans³. Since the accumulation of snow at the South Pole is 8 g/cm²/yr., it follows that the yearly infall of nitrogen as NO_3' and NO_2' is 5×10^{-8} g/cm²/yr., which is 0.005 kg/hectare or 0.0045 lb./acre.

Another possible source of this material is extraterrestrial. Whipple⁴ has reviewed the evidence for the infall of meteoric material and gives an accretion of 1,000 tons of meteoric material per day for the whole Earth, which is 0.007 kg/hectare. This is inadequate to provide the amounts of fixed nitrogen observed.

The conclusion from this work is that the annual infall of nitrogen as nitrate and nitrite at the South Pole due to geophysical phenomena in the upper atmosphere is less than, or equal to, 0.005 kg/hectare (0.0045 lb./acre).

This work was supported by the New Zealand University Grants Committee and the Victoria University of