the Materials Research Laboratory, Pennsylvania State University, has informed us that his study of the FeK absorption edge shows more than 90 percent of the iron to be in the ferric state.

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Ferrosilite ($FeSiO_3$): Synthesis at High Pressures and Temperatures

Abstract. *The $FeSiO_3$ (ferrosilite) end member of the pyroxene series is not known as a pure mineral in nature and cannot be synthesized at atmospheric pressure. It is readily synthesized, however, at pressures from 18 to 45 kb and temperatures from 1150° to 1400°C. Its refractive indices approach those predicted for ferrosilite and it melts incongruently to an Fe_2SiO_4-rich liquid plus quartz.*

Under high pressures and temperatures ferrosilite ($FeSiO_3$, with the pyroxene structure) has been synthesized for the first time. It has also been synthesized independently by S. Akimoto and colleagues at the University of Tokyo. Although $FeSiO_3$ is an important constituent of many pyroxenes, it occurs rarely if at all as a discrete phase. The only suspected occurrence is in lithophysae of some obsidians, where pyroxenes are found whose optical properties are similar to those extrapolated to $FeSiO_3$ from pyroxene solid solutions (*1*); their scarcity and small grain size have prevented chemical analysis.

Attempts at experimental synthesis, either in evacuated tubes or in controlled atmospheres at low pressures, have failed. Starting materials with the bulk composition $FeSiO_3$ crystallize to fayalite (Fe_2SiO_4) plus SiO_2 (*2*). Bowen has suggested the possibility that fayalite grows metastably, thus masking ferrosilite stability (*1*).

We first made ferrosilite during preliminary runs to determine the stability of fayalite in crimped but unsealed platinum capsules in single-stage piston-and-cylinder high-pressure apparatus. Inasmuch as the internal heating element of the apparatus is a graphite sleeve, the reaction $2C + O_2 = 2CO$ might buffer the partial pressure of oxygen in the capsule, thus reducing the fayalite to SiO_2 plus metallic Fe. After several hours at 20 kilobars and 1250°C, the charge was mainly fayalite with minor magnetite and a phase thought to be ferrosilite from its optical properties. Apparently, loss of Fe by alloying with the platinum container, with concomitant oxidation of some FeO to magnetite, drove the bulk composition of the iron silicate slightly toward $FeSiO_3$.

The identification of ferrosilite was confirmed by runs made on the $FeSiO_3$ composition. Proper proportions of Fe, Fe_2O_3, and SiO_2 were reacted in an evacuated silica glass tube to yield an equimolar mixture of fayalite and quartz. This material was packed in Fe capsules with tightly fitting lids and used in high-pressure runs. The new phase was synthesized under conditions ranging from 1150°C at 18 kb to 1400°C at 45 kb (Table 1). Reaction was nearly complete, with small amounts (1 to 5 percent) of fayalite plus quartz or coesite apparently shielded by inclusion in the major phase. Thus the composition of the new phase must lie near $FeSiO_3$. The presence of the Fe capsule suggests that the Fe_2O_3 content, if any, should be small.

Ferrosilite melts incongruently in the range 20 to 40 kb to an Fe_2SiO_4-rich liquid plus quartz; melting relations at higher pressures have not yet been determined. The liquid quenches rarely to glass and more commonly to fayalite or to fayalite plus ferrosilite with a distinctive texture. Ferrosilite synthesized just below the incongruent melting temperature is orthorhombic; this inverts in a few hours at room temperature and pressure to a polysynthetically twinned monoclinic form. It is not yet clear whether the orthorhombic polymorph forms stably or metastably. At temperatures roughly 100°C below that of incongruent melting, ferrosilite crystallizes as a monoclinic form in which twinning is simple or absent.

Preliminary optical properties for the monoclinic form are:

$$n_X = 1.764 \pm 0.002$$
$$n_Y = 1.767 \pm 0.002$$
$$n_Z = 1.792 \pm 0.002$$
$$Z \wedge c = 31° \pm 1°$$
$$(+)2V = 25° \pm 5°$$

where n_X, n_Y, and n_Z are the principal indices of refraction, $Z \wedge C$ is the angle between the principal optic direction Z

Table 1. Results of selected runs on $FeSiO_3$ composition with different starting materials. Explanation of abbreviations: fay, fayalite; qtz, quartz; fs, ferrosilite; coes, coesite; quench, quench products including glass, fayalite, and ferrosilite.

P (kb)	T (°C)	Duration (hr)	Results
	Fayalite and quartz		
18	1150	23	fs; minor fay, qtz
20	1200	14	fs; minor fay, qtz
20	1300	14	qtz + quench
30	1300	1	fs; minor fay, qtz
30	1400	1	qtz + quench
40	1400	1	fs
40	1450	1	qtz + quench
	Fayalite and coesite		
45	1400	1	fs
	Ferrosilite		
14	1000	31	fay + qtz + fs

and the crystallographic direction c, and $2V$ is the optic angle. For the orthorhombic form:

$$n_X = 1.772 \pm .003$$
$$n_Y = 1.780 \pm .002$$
$$n_Z = 1.789 \pm .002$$
$$(+)2V = 58° \pm 5°$$

A prominent prismatic cleavage yields fragments whose orientation prevents accurate determination of $2V$ in oil mounts. Monoclinic ferrosilite is clear or has a slight greenish tint; the orthorhombic form is faintly pleochroic in tints of green and yellow green.

Powder difractometer patterns of the two polymorphs (Table 2) are roughly similar to those of monoclinic and orthorhombic enstatite; the lines are all shifted to larger d values. A strong preferred orientation of grains on the powder mounts affects the relative intensities in Table 2. The pattern for the orthorhombic form is more like that of orthoenstatite than that of protoenstatite.

Molar volumes of various assemblages with $2FeSiO_3$ bulk composition are given in Table 3 (*3*). It is clear that high pressures should favor the formation of ferrosilite over fayalite plus quartz, if the entropy change of the reaction is not greatly dependent on pressure and if the compressibilities of the two assemblages are approximately equal. Ferrosilite breaks down to fayalite plus quartz at 1000°C and 14 kb but can be synthesized from that assemblage at 1150°C and 18 kb (Table 2); hence pressure does determine the stability of ferrosilite in that temperature range. As more data on the lower stability of ferrosilite are acquired, it may be possible to extrapolate the boundary curve to low pressures, thus providing a check on Bowen's suggestion of possible stability at 1 atm. The molar volume of fayalite plus coesite is closely similar to that of ferrosilite (Table 3), and whereas ferrosilite has been synthesized in the low-pressure portion of the coesite stability field (*4*) (1400°C, 40 and 45 kb), it is possible that fayalite plus coesite might be stable at some higher pressures. Ferrosilite is expected to break down once the field of Fe_2SiO_4 spinel is reached (*5*).

Table 2. Preliminary x-ray data for ferrosilite: unfiltered iron radiation; silicon internal standard; θ is the Bragg angle of reflection.

2θ (FeKα) (deg)	I	hkl	
Monoclinic polymorph			
17.22	4	110	
24.27	6	020	
33.64	8	021	
34.85	8	220	
37.22	10	221	
38.86	6	310	
43.64	3	131	(?)
43.80	2	202	(?)
45.93	2	002	
46.02	2	221	
53.22	2	331 330	
56.70	2	041	
Orthohombic polymorph			
17.17	7	120	
24.21	10	020	
33.66	4	121	
34.81	7	420	
37.75	1	321	
38.85	9	610	
41.22	2	421	
43.78	2	131	
45.36	2	202 430 521	
47.44	1	331	
49.74	2	800	
53.95	2	630 502 322 531	
58.05	2	440 241	

Table 3. Molar volumes of assemblages with $2FeSiO_3$ composition.

Assemblage	Molar volume (cm^3/mole)
Fayalite (46.41) + quartz (22.68)	69.09
Fayalite + coesite (20.75)	67.16
2 Ferrosilite (33.44)	66.88 ± 1.32
Fe_2SiO_4 spinel (42.02) + coesite	62.77
Fe_2SiO_4 spinel + stishovite (14.02)	56.04

Data on the synthesis and stability of ferrosilite may not be of direct significance in petrology, for the only suspected occurrences of the mineral are from low-pressure environments, and iron-rich pyroxenes are unlikely to occur in the mantle. Nevertheless, optical, structural, and thermodynamic data from the $FeSiO_3$ end member will be most useful in studies of the pyroxene group. Furthermore, the behavior of ferrosilite under pressure may serve as a model for enstatite, probably an important mantel mineral, as fayalite serves for forsterite. Ferrosilite synthesized at high pressures will also be useful for stability experiments at low pressures (*6*).

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Group Learning of Speech Sequences without Awareness

Abstract. *Speech sequences in groups of three persons each were registered by throat microphones and voice relays. These and other automatic devices were used to program differential reinforcement of given speech sequences with a modified conditioning technique. The results show that the order of speakers in a discussion can be brought under partial experimental control with accompanying changes in the role behavior of individuals.*

A significant part of human social behavior consists of the verbal interaction of persons in small groups, and a great deal of research has been directed toward identifying and describing its basic features. Both the meaning and the physical attributes of verbal exchange have been studied as well as its implications for leadership and other aspects of group behavior (*1*).

The research reported herein is concerned with the sequence of speeches in a group discussion and the question whether this systematic property of verbal interaction, if treated as a free operant, can be manipulated through differential reinforcement (*2*). Familiar examples often noted in groups are: who talks after whom, who has the last word, who butts in, who starts off, who is silent, and so on. In contrast to previous research on verbal conditioning in individuals (*3*), in this experiment one could determine whether the conversational order of several in-