that we are observing plasmas in which the distribution of ion states departs radically from thermal equilibrium for the local electron temperature, and that a minimum of two parameters, that is, electron temperature and degree of departure from ionization equilibrium as functions of position, must be employed to describe local plasma conditions. This departure from ionization equilibrium is also apparent in the class 3b flare shown in Fig. 8, where continuum slope measurements again indicate electron temperatures of 20 × 10^6 °K or more, while no appreciable intensity of the helium-like iron and hydrogen-like calcium line emission is produced.

It is interesting to note the absence of the Fe K-emission in Fig. 10 at the same time that strong continuum is observed to extend well beyond the K critical excitation energy. Although the cross-section for K line excitation of Fe is about an order of magnitude less than for the lighter elements Ca, Si, S, and Mg in the 1 to 15 kev range, this factor alone does not appear to be sufficient to explain the absence of the K lines of Fe. A quantitative treatment of this problem may provide a measure of the relative abundance of Fe in the flare region.

The picture of the flare process that may be emerging is one in which rapid local heating of plasma electrons occurs, with energy possibly derived from the self-inductance of a disturbed electrical current system as suggested by Alfvén and Carlqvist (*8*). The departure from ionization equilibruim may then derive either from the low pressure of the plasma region involved or from the rapidity with which the inductively driven current expands into successive and still "cool" plasma regions, possibly as a result of instabilities which successively choke off the conductivity along each preferred path.

Table 1. Transitions and wavelengths on 1 January 1968, 0415 U.T.

Ion	Transitions	Wavelength (Å)	Ref.
Al V	K	8.33	(*3*)
Al VI	K	8.26	(*3*)
Al VII	K	8.22	(*3*)
Al VIII	K	8.14	(*3*)
Al IX	K	8.06	(*3*)
Al X	K	7.97	(*3*)
Al XI	K	7.87	(*3*)
Al XII	$1s^2$-$1s2p$	7.75	(*3,9,10*)
Al XIII	$1s$-$2p$	7.17	(*5*)
Ca XVII	K	3.22	(*3,10*)
Ca XVIII	K		
Fe XXIV	$1s^22s$-$1s^24p$	8.06	(*10*)
Fe XXIV	$1s^22s$-$1s^25p$	7.22	(*10*)
Mg XI	$1s^2$-$1s3p$	7.85	(*9,10*)
Mg XI	$1s^2$-$1s4p$	7.47	(*9,10*)
Mg XI	$1s^2$-$1s5p$	7.31	(*8*)
Mg XII	$1s$-$2p$	8.42	(*5*)
Mg XII	$1s$-$3p$	7.10	(*5*)
Mg XII	$1s$-$4p$	6.73	(*5*)
Si IX	K	6.95	(*3*)
Si X	K	6.87	(*3*)
Si XI	K	6.81	(*3*)
Si XII	K	6.73	(*3*)
Si XIII	$1s^2$-$1s2p$	6.68	(*3,10*)
Si XIII	$1s^2$-$1s3p$	5.67	(*10*)
Si XIII	$1s^2$-$1s4p$	5.40	(*10*)
Si XIV	$1s$-$2p$	6.18	(*5*)
Si XIV	$1s$-$3p$	5.21	(*5*)
Si XIV	$1s$-$4p$	4.94	(*5*)
S XV	$1s^2$-$1s2p$	5.04	(*3,10*)
Unidentified		8.28 8.31	

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Composition of Aqueous Solutions in Equilibrium with Sulfides and Oxides of Iron at 350°C

Abstract. *Solutions of potassium chloride* (p*H-buffered and 1-molal*) *equilibrated at 350°C with pyrrhotite, pyrite, and magnetite contained approximately 1 millimole of reduced sulfur and less than 0.1 millimole of oxidized sulfur per kilogram. Similar solutions equilibrated with pyrite, magnetite, and hematite contained approximately 1 millimole of reduced sulfur, but 3 to 6 millimoles of oxidized sulfur per kilogram. Both types of solutions contained less than 0.1 millimole of iron per kilogram at* p*H* $\geqslant$ *6 and approximately 100 millimoles per kilogram at* p*H 2.*

The oxidation state and concentration of sulfur and of iron in typical hydrothermal solutions from which metallic ores are precipitated have long been debated. We here report on the composition of *p*H-buffered solutions in equilibrium with the assemblages pyrrhotite (Fe_7S_8 to Fe_9S_{10})–pyrite (FeS_2)–magnetite (Fe_3O_4) and pyrite–magnetite–hematite (Fe_2O_3). These assemblages were placed in gold capsules with approximately 3 ml of KCl, KCl–HCl–K_2SO_4, or KCl–Na_2S solution, and with either the assemblage potassium feldspar ($KAlSi_3O_8$)–muscovite [$KAl_3Si_3O_{10}(OH)_2$]–quartz (SiO_2), or the assemblage muscovite–kaolinite [$Al_2Si_2O_5(OH)_4$]–quartz. The capsules were flushed with nitrogen, welded shut, placed in a reaction vessel, and held at 350°C under a confining pressure of 270 atm for periods up to 64 days. At the end of each experiment the reaction was quenched rapidly, the solid phases were x-rayed, and the solution was analyzed.

Runs charged with potassium feldspar, muscovite, and quartz contained only these silicate phases after quenching. On the other hand, most of the runs charged with muscovite, kaolinite, and quartz contained no kaolinite or pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] detectable by x-ray after quenching. Natural, monoclinic pyrrhotite was used as a starting material. Its composition, as determined by the method of Arnold and Reichen (*1*), was $Fe_{6.95}S_8$. At the end of each experiment pyrrhotite had inverted to the hexagonal form with a composition near Fe_9S_{10}, in good agreement with the data of Toulmin and Barton (*2*). No changes were detected in the x-ray traces of the pyrite, magnetite, and hematite which were used as starting materials.

A few drops of solution were extracted with a hypodermic needle for measurement of the *p*H in a Beckman "one-drop" *p*H electrode assembly. Additional portions of solution were withdrawn for determination of the concentration of iron, total reduced sulfur, and total oxidized sulfur. Iron was determined by atomic absorption spectrometry. Reduced sulfur was precipitated as ZnS and iron sulfide in alkaline medium. The precipitated sulfides were separated from the solution and were oxidized with a mixture of NaOH and H_2O_2. The resulting sulfate was precipitated as $BaSO_4$ from a $BaCl_2$ solution containing Ba^{133}; the gamma activity of the precipitate was determined with a single-channel gamma-ray spectrometer. Oxidized sulfur in the filtrate from the sulfide separation procedure was precipitated with the radioactive $BaCl_2$ solution. The concentration of total dissolved sulfur (determined as $BaSO_4$ in a separate portion of solution from each run) was generally within 10 percent and always within 20 percent of the sum of the separately determined concentrations of reduced and oxidized sulfur.

Our data for runs with the assemblage pyrrhotite–pyrite–magnetite are summarized in Table 1. The concentration of reduced sulfur in 1-molal KCl solutions in equilibrium with these iron minerals and buffered either by the assemblage potassium feldspar–muscovite–quartz or by the assemblage muscovite–kaolinite(?)–quartz lies between 1.1 and 2.1 mmole/kg. The concentration of oxidized sulfur in equilibrium with these assemblages is less than 0.1 mmole/kg. Solutions with initially high concentrations of Na_2S tended not to equilibrate with the buffer assemblages and produced quantities of apparently metastable oxidized sulfur. Anomalous oxidized sulfur was also observed in experiments lasting 1 to 10 months at 250°C with the assemblage pyrrhotite–pyrite–magnetite.

Table 1. Composition of solutions equilibrated with pyrrhotite, pyrite, and magnetite.

Run No.	Initial composition of solution in addition to 1-molal KCl	Time (days)	*p*H	Reduced sulfur (mmole/kg)	Oxidized sulfur (mmole/kg)	Iron (mmole/kg)
	With potassium feldspar–muscovite–quartz buffer					
1	None	41	6.0 → 3.55	0 → 1.1	0 →< 0.1	0 → 5.2
2	0.01*m* HCl, 0.01*m* K_2SO_4	57	2.05 → 4.31	0 → 1.1	10 → 0.4	0 → 2.1
3	0.1*m* Na_2S	14	12.25 → 9.45	100 → 77	0 → 12	0 →< 0.1
4	0.1*m* Na_2S	58	12.25 → 8.80	100 → 67	0 → 29	0 →< 0.1
	With muscovite–kaolinite(?)–quartz buffer					
5	None	41	6.0 → 3.31	0 → 2.1	0 →< 0.1	0 → 57
6	None	50	6.0 → 2.60	0 → 1.7	0 →< 0.1	0 → 340
7	0.01*m* HCl, 0.01*m* K_2SO_4	57	2.05 → 2.80	0 → 1.7	10 → 0.2	0 → 68
8	0.01*m* Na_2S	64	11.50 → 4.75	10.0 → 5.8	0 →< 0.1	0 → 25 (?)
	Without silicate buffer					
9	None	34	6.0 → 5.60	0 → 2.8	0 → 0.47	0 → 0.32
10	0.01*m* Na_2S	64	11.50 → 7.55	10.0 → 3.7	0 → 7.3	0 →< 0.1

Table 2. Composition of solutions equilibrated with pyrite, magnetite, and hematite.

Run No.	Initial composition of solution, in addition to 1-molal KCl	Time (days)	*p*H	Reduced sulfur (mmole/kg)	Oxidized sulfur (mmole/kg)	Iron (mmole/kg)
	With potassium feldspar–muscovite–quartz buffer					
1	None	14	6.0 → 4.40	0 → 0.65	0 → 7.4	0 → 2.5
2	None	60	6.0 → 4.10	0 → 0.65	0 → 3.0	0 → 6.5
3	0.01*m* HCl, 0.01*m* K_2SO_4	40	2.05 → 2.80	0 → 1.30	10 → 6.2	0 → 6.6
4	0.01*m* HCl, 0.01*m* K_2SO_4	60	2.05 → 2.80	0 → 1.50	10 → 7.0	0 → 2.6
5	0.1*m* Na_2S	58	12.25 → 6.40	100 → 1.2	0 → 9.2	0 →< 0.1
	With muscovite–kaolinite(?)–quartz buffer					
6	None	10	6.0 → 2.35	0 → 2.7	0 → 2.1	0 → 59
7	None	50	6.0 → 1.70	0 → 0.80	0 → 28 (?)	0 → 340
8	0.01*m* HCl, 0.01*m* K_2SO_4	10	2.05 → 1.95	0 → 1.7	10 → 9.0	0 → 96

Table 3. Composition of solutions in runs containing no iron minerals equilibrated with the assemblage potassium feldspar–muscovite–quartz buffer.

Run No.	Initial composition of solution, in addition to 1-molal KCl	Time (days)	*p*H	Oxidized sulfur (mmole/kg)	Iron (mmole/kg)
1	None	43	6.0 → 5.05		
2	0.01*m* HCl	43	2.09 → 3.15		
3	0.01*m* HCl, 0.01*m* K_2SO_4	34	2.05 → 2.45	10 → 9.9	
4	0.01*m* $FeCl_2$	34	5.50 → 4.28		10 → 10

The concentration of iron in solutions from runs containing pyrrhotite, pyrite, and magnetite increases dramatically with decreasing *p*H. The partially equilibrated Na_2S (runs 3 and 4, Table 1) contained less than 0.1 mmole of iron per kilogram, whereas run 6, whose final *p*H was 2.60, contained 340 mmole of iron per kilogram.

The variability at room temperature of the *p*H of the runs for the Hemley (*3*) *p*H-buffer assemblages (Table 1), as well as that in Tables 2 and 3, is due in part to lack of equilibration, in part to the loss of initial kaolinite during equilibration, and probably also to the effect of the dissociation of a variety of ionic complexes during cooling. The dissociation of complexes such as HSO_4^- reduces the *p*H of solutions during cooling, whereas the dissociation of complexes such as $FeOH^+$ increases the solution *p*H.

Our data for experiments with pyrite, magnetite, and hematite are summarized in Table 2. The concentration of total reduced sulfur in solution is between 0.6 and 2.7 mmole/kg; that is, it is similar to that of solutions in equilibrium with pyrrhotite, pyrite, and magnetite. On the other hand, the concentration of oxidized sulfur is 3 to 6 mmole/kg since the oxygen fugacity in equilibrium with the assemblage pyrite–magnetite–hematite is four orders of magnitude greater than that in equilibrium with the assemblage pyrrhotite–pyrite–magnetite. The concentration of iron in equilibrium with these two assemblages is similar at equivalent values of the *p*H at room temperature.

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