Experimental Studies of the Synthesis of Pyrite and Marcasite (FeS_2) from 0° to 200° C and Summary of Results

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ABSTRACT

Pyrite and marcasite (FeS_2) precipitation was studied experimentally from 0 to 200° C under conditions that may have existed during the formation of carbonate-hosted Pb-Zn (Mississippi Valley Type) deposits. Dissolved ferrous iron (from $FeSO_4$ or $FeCl_2$), elemental sulfur (S°), and hydrogen sulfide (H_2S) were the reactants, with sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) added to adjust the initial pH to 3.2 or less. A separate series of experiments using added $CaCO_3$ was run to examine the acid-neutralizing effect of $CaCO_3$ on FeS_2 formation. Reaction times were from 1 to 110 hours with most reactions conducted for 24 hours. On the time scale of these experiments, iron disulfides did not form or formed in small amounts at temperatures of 150° C or less, whereas larger yields of disulfides were obtained at 200° C. In many instances, very pure disulfide phases were produced ($\geq$95 weight percent FeS_2 as marcasite or pyrite).

Marcasite was usually the dominant disulfide mineral produced when both H_2S and S° were initially present in acid-sulfate solutions (50-95 weight percent of $FeS_{2(total)}$, where $FeS_{2(total)}$=pyrite + marcasite). Nearly pure marcasite (90 to >95 weight percent of $FeS_{2(total)}$) formed in acid-sulfate solutions when only S° (not H_2S) was added. Over the range of 0.005-0.20 M H_2SO_4, increasing acidity of the solution promoted marcasite formation over pyrite. Beyond a total H_2SO_4 concentration of 0.20 M, however, the marcasite fraction of $FeS_{2(total)}$ decreased. At an H_2SO_4 concentration of 0.24 M, only a trace of FeS_2 formed (pyrite) and marcasite was not detected. A similar trend was found in acid-chloride solutions over the HCl concentration range of 0.005-0.03 M, where the marcasite fraction was 57-92 weight percent of $FeS_{2(total)}$. However, $FeS_{2(total)}$ and weight percent marcasite maxima were reached at 0.01 M HCl, and then decreased as the HCl molarity increased to 0.03 M.

Pyrite and marcasite were produced from ferrous chloride or ferrous sulfate solutions in the presence of $CaCO_3$ (without added acid or H_2S), but pyrite was usually the dominant disulfide (greater than 50 weight percent of $FeS_{2(total)}$). Minerals formed in these experiments in addition to disulfides include iron monosulfide, anhydrite, gypsum, siderite, magnetite, and hematite. Marcasite comprised 50 weight percent or more of $FeS_{2(total)}$ in only 2 of the 15 $CaCO_3$ experiments. In the other 13 experiments, marcasite did not exceed 33 weight percent in 7 experiments and was not detected in the other 6 experiments. Thus, the presence of $CaCO_3$ apparently decreases the relative amount of marcasite produced. The results are consistent with the fact that marcasite usually forms at pH values less than 5 and that pyrite tends to be the dominant disulfide formed at higher pH values.

INTRODUCTION

Pyrite and marcasite (iron disulfide, FeS_2) coexist in Mississippi Valley Type (MVT) carbonate-hosted Pb-Zn deposits. Much interest centers on sulfide minerals as indicators of processes that result in formation of MVT and other sulfide ore deposits (Cathles and Smith, 1983). It is of particular interest to explain how marcasite can form and persist in a carbonate host rock because experimental evidence indicates that marcasite requires a pH less than 5 to form (Goldhaber and Stanton, 1987; Murowchick, 1984). Different generations of iron disulfides formed and persisted during emplacement of MVT deposits (Heyl and others, 1959). Pyrite formation may have formed voids isolated from carbonate host-rock where marcasite formation could take place. Petrographic studies from different MVT ore districts bear out this sequence of pyrite formation followed by marcasite formation (Heyl and others, 1959). An additional interest in pyrite and marcasite is that the geochemical conditions under which both FeS_2 dimorphs form and coexist are not completely understood. Pyrite is found in nearly every geologic environment and is therefore an important mineral in the global sulfur cycle (Berner, 1970). Marcasite, on the other hand, is much rarer and limited to a few geochemically extreme environments (Murowchick and Barnes, 1987).

A series of experiments was designed to understand some chemical controls on the formation of pyrite and marcasite at temperatures and acidities postulated for formation of MVT-type deposits. Stable isotope geothermometry (Barnes, 1979; Heyl and others, 1974) and fluid inclusion data (Roedder, 1977; Rowan and Leach, 1990) show evidence that temperatures approaching 200° C were attained in MVT deposits, and P_{CO_2} values from fluid inclusions indicate that the pH of some solutions may have been less than 5 (Leach and others, 1991). In this report, we describe the apparatus and procedures used to synthesize and purify pyrite and marcasite, and methods to determine the mineralogy of the solid reaction products and chemical composition of the reaction solution. Tabulated data from 95 different experiments and some preliminary analysis of the results are presented in this report.

EXPERIMENTAL METHODS

Due to the variety of conditions employed in this study, it is convenient to refer to three major series of experiments. The first series (sulfate series) comprised the majority of the experiments and utilized ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sulfuric acid (H_2SO_4), elemental sulfur (S°), and hydrogen sulfide (H_2S) as reactants. The second, less extensive series (chloride series) used ferrous chloride ($FeCl_2 \cdot 4H_2O$) and hydrochloric acid (HCl) in addition to S° and H_2S. The third series used added $CaCO_3$ with either iron source and S°, but without acid or H_2S, and are referred to as the calcite series. Within each major group, modifications of the reagent concentrations and reaction conditions were made and will be described in later sections. Tables 1, 2, and 3 detail reaction conditions for the sulfate, chloride, and calcite series, respectively.

Autoclave and Vessel Preparation

A 250 mL capacity Berghof autoclave (figure 1) capable of incremental heating to 250° C (±10° C) was used in all experiments. The removable inner Teflon reaction vessel and stainless steel liner are placed inside the heating jacket; temperature control is maintained by a thermocouple probe inserted through the autoclave top. Pressures as high as 20 bars were recorded in early experiments, but H_2S corrosion of the internal pressure gauge components ultimately resulted in irreproducible pressure readings. Hydrogen sulfide corrosion also caused rapid failure of the nickel-metal pressure release disc and leakage of the reaction solution in early experiments. The rate of disc failure was reduced by coating the disc with Teflon paste and then overlaying the disc with a similar-sized piece of .016-inch thick Teflon.

The Teflon vessel was degassed in a vacuum oven at 90° C for at least 48 hours to remove oxygen that may have been present in pore spaces. However, vessels used in experiments prior to number 40 were not degassed and entrapped O_2 may have contributed to formation of minor amounts of hematite in some experiments. The importance of outgassing O_2 from these vessels has been described by Wanty and Goldhaber (1985). An ice-filled dessicator was used to cool the vessel to 0° C to increase the solution H_2S concentration (Millero, 1986). During solution preparation, N_2 flowed through the dessicator to exclude air from the vessel to prevent oxidation of Fe^{2+} and H_2S. Reagent grade chemicals and deoxygenated, distilled water were used in all experiments.

Electrometric measurement or control of pH during an experiment was not possible; however, qualitative pH measurement with litmus paper was made before and after reaction in some experiments. The pH during reaction was calculated using the computer program PHREEQE (Parkhurst and others, 1980), an equilibrium geochemical model that can be used to determine pH based on changes in solution and mineral chemistry. Data used to perform these calculations was obtained from the known solution composition before reaction, analytically-determined solution composition after reaction, product mineral compositions and abundances, and reaction stoichiometry based on chemical analyses.

Reaction Solution Preparation

Sulfate series

In the sulfate series, a sufficient volume of distilled water was deoxygenated with ultra high-purity N_2 for 12 hours, then 150 mL was added to the Teflon vessel. The vessel was capped with a rubber stopper equipped with a gas sparger, then ultra high-purity N_2 was bubbled

Table 1. Reactant concentrations, reaction conditions, and results for sulfate series experiments.

Exp #	H_2SO_4 (M)	$FeSO_4$ (g)	S^o (g)	H_2S (%Sat)	Temp (C^o)	Time (hrs)	Wt. S^o recovered(g)	Wt. FeS_2 recovered(g)	Wt.%FeS_2 as Marcasite	Wt.%FeS_2 as Pyrite
3	0.03	7.5	0.75	100	200	24	ND	ND	50*	50*
6	0.02	7.5	0.75	100	200	24	0.089	1.83	44	58
7	0.0006	7.5	0.75	10	200	24	0.078	1.12	79	21
9	0.16	7.5	0.75	100	200	24	0.35	1.67	91	9
10	0.20	7.5	0.75	100	200	24	0.5	1.45	>95	<5
11	0.10	7.5	0.75	100	200	24	0.12	1.71	87	33
12	0.12	7.5	0.75	100	200	24	0.29	1.32	89	11
13	0.24	7.5	0.75	100	200	24	0.601	0.028	ND	ND
14	0.22	7.5	0.75	100	200	24	0.34	0.7	92	8
15	0.07	7.5	0.75	100	200	24	0.19	2.02	53	47
16	0.00	2.05g FeS	0.75	0	200	24	ND	ND	67*	33*
17	0.07	7.5	0.75	10	200	24	0.1	0.915	93	7
18	0.00	2.05g FeS	2.25	0	200	24	ND	ND	29*	71*
19A	0.16	7.5	0.75	100	0	H/C	all S	0	0	0
19B	0.16	7.5	0.75	100	50	H/C	all S	0	0	0
19C	0.18	7.5	0.75	100	75	H/C	all S	0	0	0
19D	0.18	7.5	0.75	100	100	H/C	all S	0	0	0
19E	0.18	7.5	0.75	100	150	H/C	all S	0	0	0
19F	0.18	7.5	0.75	100	200	H/C	0.71	0.106	84	16
19G	0.18	7.5	0.75	100	200	72	0.31	1.5	88	12
20A	0.07	7.5	0.75	100	5	H/C	all S	0	0	0
20B	0.07	7.5	0.75	100	50	H/C	all S	0	0	0
20C	0.07	7.5	0.75	100	75	H/C	all S	0	0	0
20D	0.07	7.5	0.75	100	100	H/C	all S	0	0	0
20E	0.07	7.5	0.75	100	150	H/C	mostly S	tr FeS2	tr	tr
20F	0.07	7.5	0.75	100	200	H/C	0.71	0.14	32	68
20G	0.18	7.5	0.75	100	200	72	0.21	1.77	48	52
21	0.16	7.5	0.75	100	200	24	0.29	0.87	93	7
22A	0.0006	0.75	0.75	100	200	24	0.46	0.28	74	26
22B	0.04	0.75	0.75	100	200	24	0.004	0.277	87	13
22C	0.07	0.75	0.75	100	200	24	0.058	0.007	92	8
22D	0.11	0.75	0.75	100	200	24	0.602	0.002	ND	ND
23	0.11	7.5	0.75	10	200	24	0.46	0.15	94	6
24	0.04	7.5	0.75	10	200	24	0.21	0.86	>95	<5
25	0.09	7.5	0.75	10	200	24	0.3	0.5	93	7
27A	0.07	7.5	0.75	100	150	1	mostly S	tr FeS2	tr	tr
27B	0.07	7.5	0.75	100	150	3	0.66	0.13	57	43
27C	0.07	7.5	0.75	100	150	5	ND	ND	ND	ND
27D	0.07	7.5	0.75	100	150	25	0.6	0.46	80	20
27E	0.07	7.5	0.75	100	150	64	0.55	0.78	74	26
28A	0.07	7.5	0.75	100	200	1	0.73	0.010	45	55
28B	0.07	7.5	0.75	100	200	3	0.53	0.87	79	21
28C	0.07	7.5	0.75	100	200	5	0.48	0.85	79	21
28D	0.07	7.5	0.75	100	200	24	0.19	1.78	64	38
28E	0.07	7.5	0.75	100	200	110	0.022	1.062	>95	<5

Table 1, continued

Exp #	H_2SO_4 (M)	$FeSO_4$ (g)	S^o (g)	H_2S (%Sat)	Temp (C°)	Time (hrs)	Wt. S^o recovered(g)	Wt. FeS_2 recovered(g)	Wt.%FeS_2 as Marcasite	Wt.%FeS_2 as Pyrite
28F	0.07	7.5	0.75	100	200	18	ND	ND	ND	ND
28EII	0.07	7.5	0.75	100	200	95	0.046	1.137	>95	<5
29	0.07	7.5	0.75	100	200	24	0.166	0.982	>95	<5
28FII	0.07	7.5	0.75	100	200	19	0.329	0.656	>95	<5
30	0.07	7.5	0.75	100	200	24	0.19	1.39	55	45
31	0.07	7.5	0.75	100	160m	1	0.682	0	NA	NA
32	0.07	7.5	0.75	100	200	48	0.15	2.004	53	47
33A	0.07	5.63	0.56	100	200	24	0.289	1.601	66	32
33B	0.07	3.75	0.37	100	200	24	0.303	1.294	63	17
33C	0.07	1.87	0.19	100	200	24	0.531	0.669	66	14
34	0.07	7.5	0.75	100	200	72	0.219	1.988	67	33
35	0.07	7.5	0.75	100	200	12	0.22	2.018	63	37
36A	0.02	7.5	0.75	100	200	5	0.284	2.026	40	60
36B	0.02	7.5	0.75	100	200	15	0.22	2.249	61	39
36C	0.02	7.5	0.75	100	200	24	0.183	2.194	43	57
36D	0.02	7.5	0.75	100	200	48	0.13	2.067	54	46
36-0	0.02	7.5	0.75	100	200	H/C	0.401	1.415	31	69
36-1	0.02	7.5	0.75	100	200	1	0.456	1.283	28	72
36-2	0.02	7.5	0.75	100	200	2	0.396	1.157	94	6
36-3	0.02	7.5	0.75	100	200	3	0.254	1.971	44	56
37A	0.07	7.5	0	100	200	24	0.013	1.048	40	60
37B	0.03	7.5	0	100	200	24	0.016	0.902	17	83
37C	0.01	7.5	0	100	200	24	0.029	0.536	11	89
37D	.005	7.5	0	100	200	24	0.024	0.790	44	56
38A	0.16	7.5	0.75	0	200	24	0.587	0.002	ND	ND
38B	0.07	7.5	0.75	0	200	24	0.21	0.574	90	10
38C	0.03	7.5	0.75	0	200	24	0.434	0.376	89	11
38D	0.02	7.5	0.75	0	200	24	0.196	0.668	>95	<5
38E	0.01	7.5	0.75	0	200	24	0.041	1.028	>95	<5
39	0.02	7.5	0.75	0	200	74	0.014	1.046	90	10

NA=not applicable; ND=not determined; *=weight percent of marcasite and pyrite was determined on samples that contained trace impurites, usually S^O or FeS; tr=trace amount present; H/C=reactants heated to temperature and then immediately cooled.

Table 2. Reactant concentrations, reaction conditions, and results for chloride series experiments.

Exp. #	HCl (M)	NaCl (M)	$CaCO_3$ (g)	$FeCl_2$ (g)	$FeCl_2$ (M)	S^o (g)	H_2S %Sat	Temp (C°)	Time (hrs)	Wt S^o recovered(g)	Wt FeS_2 recovered(g)	Wt%FeS_2 as Marcasite	Wt%FeS_2 as Pyrite
43	0.03	2.0	0	5.367	0.18	0.75	100	200	24	0.596	0.295	57	43
45	0.01	0	0	5.367	0.18	0.75	100	200	24	0.391	1.435	92	8
46	0.01	2.0	0	5.367	0.18	0.75	100	200	24	0.633	0.651	83	17
47	0.005	2.0	0	5.367	0.18	0.75	100	200	24	0.528	0.622	92	8
48	0.015	2.0	0	5.367	0.18	0.75	100	200	24	0.492	0.452	74	26
*54	0	0	4.0	2.684	0.09	0.20	0	180	2	0.299	0.206	<5	>95
*61	0	0	4.0	2.684	0.09	0.20	0	200	2	0.031	0.314	<5	>95
*63	0	0	3.0	2.684	0.09	0.75	0	200	24	0.033	0.658	13	87
*64	0	0	3.0	2.684	0.09	0.75	0	150	24	0.069	0.946	8	92

*These experiments were run as part of the calcite series experiments which are presented in table 3. Because $FeCl_2$ was used as the iron source, these are listed here for comparison with other chloride series experiments.

Table 3. Reactant concentrations, reaction conditions, and results for calcite series experiments.

Exp #	$CaCO_3$ (g)	$FeSO_4$ (g)	$FeCl_2$ (g)	S^o (g)	Temp (C°)	Time (hrs)	Wt S^o recovered(g)	Wt FeS_2 recovered(g)	Wt%FeS_2 of total solids	Wt% FeS_2 as Marcasite	Wt% FeS_2 as Pyrite
50	1.15	7.5	-	0.75	200	24	0.017	1.147	48	63	37
51	3.0	7.5	-	0.75	200	24	0.012	1.226	24	33	67
52	3.0	7.5	-	0.75	200	2	0.169	2.665	44	70	30
53	3.0	7.5	-	0.2	200	2	0.120	0.481	15	<5	>95
54	4.0	-	2.7	0.2	180	2	0.299	0.206	5	<5	>95
55	3.0	7.5	-	0.1	200	2	ND	0.246	4	<5	>95
56	3.0	7.5	-	0.75	150	2	0.320	0.700	18	18	82
57	3.0	7.5	-	0.2	150	2	0.099	0.159	3	13	87
58	3.0	7.5	-	0.1	150	2	0.084	0.116	2	<5	>95
59	3.0	7.5	-	0.75	150	24	0.134	0.943	15	24	76
60	3.0	7.5	-	0.2	150	24	0.240	0.389	6	<5	>95
61	4.0	-	2.7	0.2	200	2	0.031	0.314	8	<5	>95
62	3.0	7.5	-	0.1	150	24	0.069	0.067	1	25	75
63	3.0	-	2.7	0.75	200	24	0.033	0.658	21	14	87
64	3.0	-	2.7	0.75	200	24	0.069	0.946	34	9	92

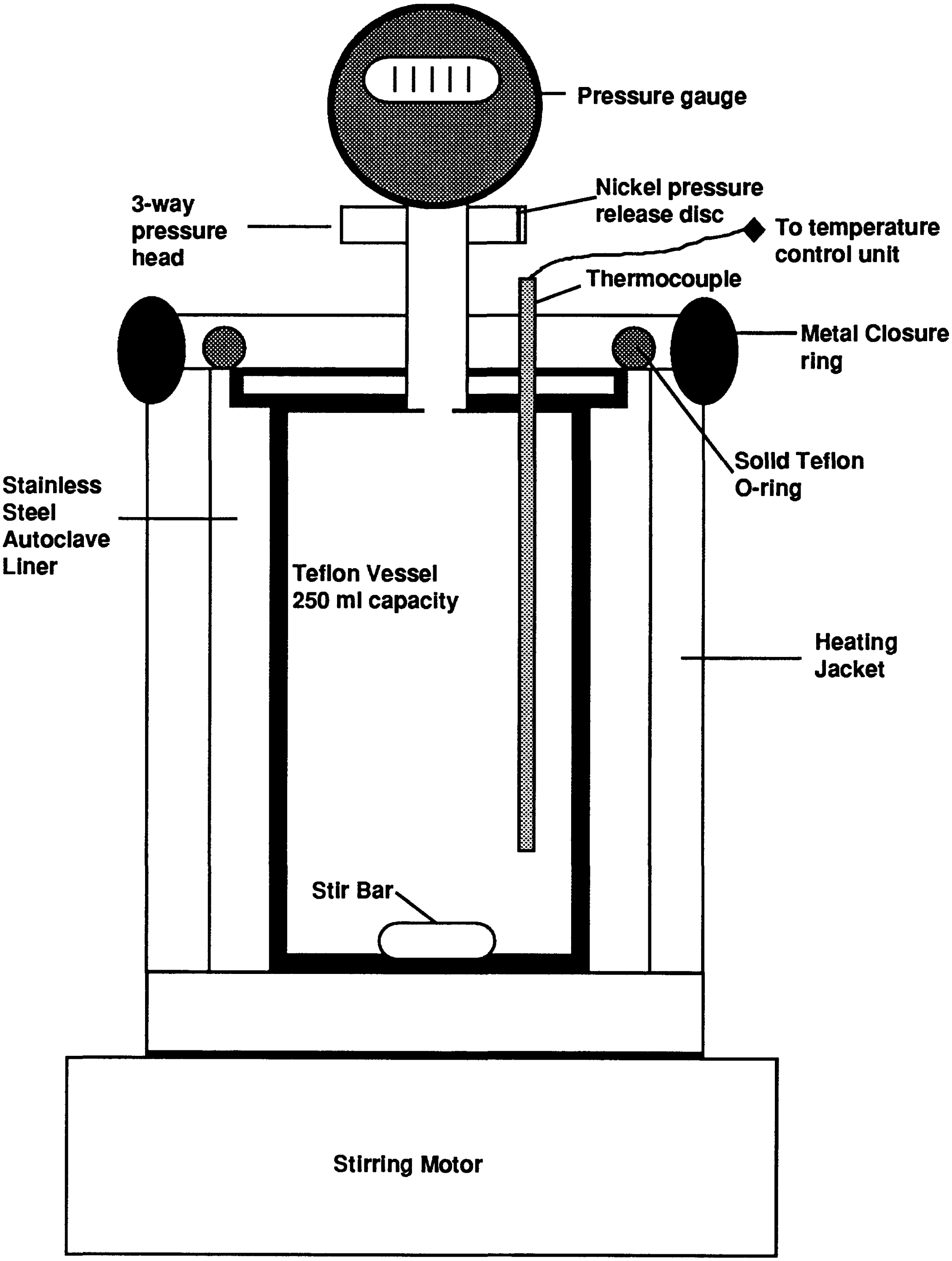

Figure 1. Diagram of reaction autoclave used in the synthesis of marcasite and pyrite over the temperature range 0-200° C.

through the water for an additional 2 hours. A motor beneath the autoclave was used to drive a magnetic stir bar inside the vessel. Stirring was begun prior to addition of reagents (to aid dissolution of the solids) and lasted for the duration of the experiment. Fresh solid ferrous sulfate ($FeSO_4 \cdot 7H_2O$), which was stored under N_2, was dissolved in the water followed by addition of the appropriate volume of concentrated H_2SO_4. Elemental sulfur was added next, then $H_2S_{(g)}$ was sparged into the solution until H_2S saturation was attained (1-5 hours). H_2S saturation was determined by titrating a series of blanks (without H_2SO_4 or HCl) with 0.05 M KOH during H_2S bubbling until the volume of added KOH necessary to neutralize the weak acid ($H_2S_{(aq)}$) became constant. Titration curves of volume of KOH added versus time were used to establish minimum sparging times necessary to saturate the solution with H_2S. $H_2S_{(g)}$ was usually bubbled into the solution for 1 to 2 hours beyond the minimum time to ensure saturation. The vessel was then immediately capped with the autoclave top and O-ring, sealed with the closure ring, and heated.

Chloride series

In the chloride series experiments, reactants were added in a manner similar to that of the sulfate series, except that some solutions were 2 M NaCl (see table 2) to mimic the postulated ionic strength and Cl^- anion dominance observed in fluid inclusions from MVT deposits (Roedder, 1977). Solid ferrous chloride ($FeCl_2 \cdot 4H_2O$, stored under N_2) was dissolved in 150 mL distilled deoxygenated water or NaCl solution and concentrated HCl was then added. Elemental sulfur was added next, followed by sparging $H_2S_{(g)}$ into the solution as in the sulfate series of experiments. Four experiments (54, 61, 63, and 64) with both $CaCO_3$ and $FeCl_2$ are listed in table 2 for comparison with other chloride series experiments, but these were run primarily as part of the calcite series experiments.

Calcite series

Experiments in which $CaCO_3$ was added were run with significantly different sets of reagents and conditions (table 3) than were the sulfate or chloride experiments. The purpose of the calcite series was to test the possibility that S° hydrolysis was capable of generating sufficient H^+ to promote marcasite formation and to determine if S° alone would significantly influence disulfide formation. Thus, acid and hydrogen sulfide were not added to the reaction solution. All but four of these experiments used $FeSO_4 \cdot 7H_2O$ with varying amounts of added S°; $FeCl_2 \cdot 4H_2O$ plus S° was used in the other four experiments. After the iron reagent had dissolved and S° was added, 3 or 4 g $CaCO_3$ was introduced into the solution, then the vessel was sealed and heated.

Heating, Reaction Times, and Cooling

Once sealed, the vessel was brought up to the desired operating temperature (tables 1-3). Heating to 200° C required about 2 hours, increasing at approximately 4 degrees per minute. Upon turning the heating unit off, the vessel was cooled from 200° to 50° C in ambient air (approximately 2 hours). Experiments were run over the range of 0-200° C to examine possible lower temperature reactions but iron disulfides formed only at temperatures at or above 150° C. Most experiments at 200° C lasted for 24 hours but ranged from 1 hour to 110 hours. The broad range of reaction times results from experiments run to examine time as the major variable. The autoclave top was removed to begin sample treatment when the temperature dropped to 50° C or less. Sampling was done only at the end of an experiment as there was no provision for withdrawing samples from the autoclave during the experiment.

ANALYTICAL METHODS

An extraction-purification method for each experimental series was developed to obtain pure disulfide(s). X-ray diffraction methods (XRD) were then used to quantify the abundances of marcasite and pyrite. Solutions were analyzed for dissolved iron, sulfate, and calcium (in $CaCO_3$ runs) to monitor the efficiency of chemical extractions, determine the extent of reaction, and to obtain chemical data for reaction modeling.

Extraction and Purification of Iron Disulfides

Sulfate series

Pyrite and marcasite were separated from the bulk solids and purified on the basis of their insolubility in 6M HCl. In many cases, the solids were mainly FeS_2 before extraction, with only minor amounts of S° and FeS present. For example, in experiment number 6, the amount of S° recovered in the solids was less than 2 percent of the total S° added at the beginning of the experiment; the remaining solids were FeS_2. This sulfur was residual S° and not a product of the reaction. The extraction-analysis scheme for the sulfate and chloride experiments is shown in figure 2. Reaction vessel contents were immediately filtered and collected on a 0.45 µm pore size Millipore filter. This filtrate was analyzed for dissolved Fe by flame atomic absorption spectrophotometry (FAAS, Fishman and Friedman, 1989). In experiments in which H_2S was not added to the acid-sulfate solution (experiments 38A-E, 39), sulfate was determined by $BaSO_4$ gravimetry. An increase in sulfate would suggest that S° hydrolysis was consuming elemental sulfur and producing additional sulfate during disulfide precipitation through the overall reaction

$$3Fe^{2+} + 4H_2O + 7S^\circ \rightarrow 3FeS_2 + SO_4^{2-} + 8H^+ \qquad \{1\}$$

Solids were weighed immediately after drying to obtain the total weight of recovered solids.

A 6M HCl leach of the solids at 25° C for 10 minutes was performed to remove iron monosulfide (FeS); this treatment does not dissolve

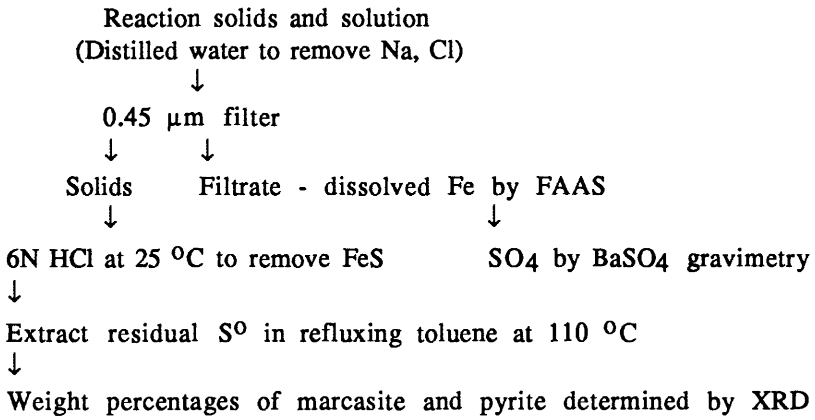

Figure 2. Diagram of the extraction and purification method used to obtain pure iron disulfide from sulfate and chloride series experiments. FAAS (flame atomic absorption spectrophotometry) and XRD (semiquantitative X-ray diffraction) methods are described in the text.

disulfides (Berner, 1964). Excess HCl was removed with a rinse of deoxygenated distilled water and the solids were then dried and reweighed to determine weight loss due to FeS removal. Because the amount of FeS was minor, analysis for iron in the filtrate from the 6M HCl leach was usually not necessary.

Next, the dried solids were refluxed in reagent grade toluene for 1-2 hours at approximately 110° C to extract S°. Generally, one reflux was sufficient to extract all sulfur; additional toluene extractions produced no further weight loss or S° detectable with X-ray diffraction or spectroscopy (see below). Additional testing indicated that the S° extraction caused a small loss of marcasite and pyrite (8 weight percent or less) which was attributed to adsorption of fine-grained FeS_2 onto glass filtration and refluxing apparatus.

Ultraviolet-visible (UV-vis) spectroscopic analysis was performed on selected samples to determine the amount of S° that dissolved in toluene during the extraction process. An aliquot of the toluene was diluted (usually 1:100) in a solution of reagent grade acetone (95 percent) plus distilled water (5 percent) and analyzed according to the method of Bartlett and Skoog (1954). $FeCl_3$ and NaCN are added to the toluene + acetone solution to form $FeSCN^{2+}$; the absorbance of this complex is measured at 465 nm and compared to the absorbance of sulfur-spiked toluene + acetone solutions to obtain the abundance of S° extracted from the solids. This analysis confirmed that the gravimetrically-determined weight loss of S° corresponded to dissolved S° from sample extractions within ±5 weight percent. As noted, X-ray diffraction of the toluene-leached solids also confirmed that S° was no longer present.

Chloride series

After the initial filtration of reaction vessel contents from experiments run with high NaCl concentrations, chloride salts were detected in the solid products. Thus, the solids were rinsed with deoxygenated distilled water and dried prior to 6M HCl treatment. Purification of the disulfides was then carried out as in the sulfate series by performing a 10-minute, 25° C 6M HCl leach and filtration, then extracting residual S° with toluene. The remaining solids were examined by X-ray diffraction analysis to determine the disulfide mineralogy and to confirm that S° was not present.

Calcite series

The extraction method was modified for experiments involving $CaCO_3$ to accomodate the different solids that formed (figure 3). Combinations of iron monosulfide (FeS), anhydrite ($CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), magnetite (Fe_3O_4), siderite ($FeCO_3$), and hematite (Fe_2O_3) were detected by XRD in the untreated solids depending on the reaction conditions. Hematite

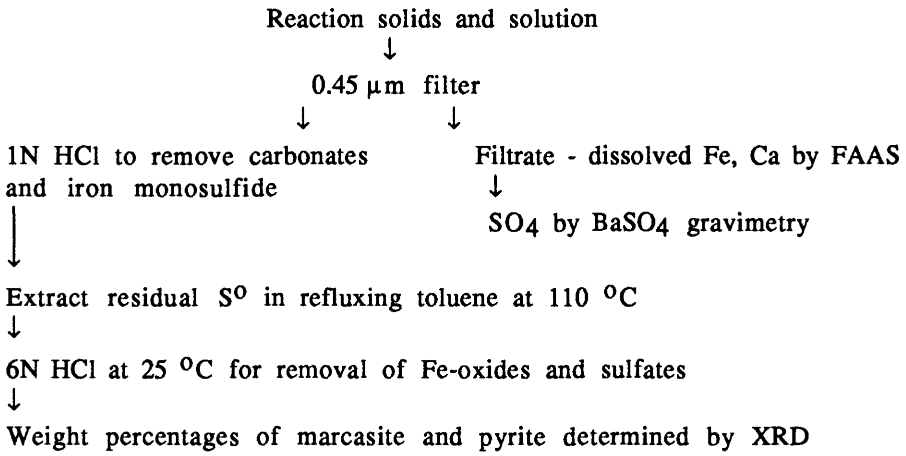

Figure 3. Diagram of the extraction and purification method used to obtain pure iron disulfide from carbonate series experiments. FAAS (flame atomic absorption spectrophotometry) and XRD (semiquantitative X-ray diffraction) methods are described in the text.

may have resulted from ferric iron in the ferrous iron reagent or Fe(III) formed by reaction of Fe(II) with O_2 in the vessel pore spaces; oxygen may also have been introduced with $CaCO_3$. However, long-term degassing of the vessel (more than 1 week) appeared to inhibit formation of hematite, but not magnetite. Thus, hematite may be an experimental artifact but magnetite is probably a true product of the reaction.

The dry raw precipitate was analyzed by XRD for mineral identification, treated with 1M HCl for 10 minutes at 25° C to remove FeS and carbonates (calcite or siderite), rinsed with deoxygenated distilled water, filtered, and dried. Some gypsum was probably dissolved by distilled water but the extent of this dissolution was not determined since the removal of these solids was the purpose of the extraction procedure. Occasionally, two such acid treatments were needed to completely remove carbonates, which consisted primarily of residual calcite; sulfates and iron oxides were not removed at this step based on XRD analysis. The 1M leach was followed by the toluene extraction for sulfur as described above. Sulfates, iron oxides, and iron disulfides were not removed by toluene as shown by XRD. The final step was the 6M HCl treatment (25° C for 20 minutes), which removed the iron oxides (magnetite and hematite) and calcium sulfates (anhydrite and gypsum). Again, two 6M HCl leaches were sometimes necessary. The residual solids consisted only of disulfide(s); in some experiments, only one of the disulfides was detected with XRD, usually pyrite. Filtrates from 1M and 6M leach steps were analyzed for iron, sulfate, and calcium by the methods described below.

Mineral Identification and Estimated FeS_2 Abundances using X-Ray Diffraction

Unextracted (raw) samples and samples from each extraction step were examined by XRD for mineral identification and to assess the efficiency of each extraction. A Philips XRG-3000 diffractometer using Cu $K\alpha$ radiation and equipped with a focusing graphite monochromator (to reduce interference from Fe fluorescence) was used to scan the samples at $2^\circ\ 2\theta$ per minute for mineral identification. Acetone-slurry mounts on petrographic slides were prepared because the small amounts of solids precluded the use of packed powder mounts.

After pure disulfide had been obtained via chemical extractions, XRD was used to quantify the proportions of pyrite and marcasite. The limit of detection of a mineral phase with XRD was >5 weight percent. Thus, if only one disulfide was present, it is reported as greater than 95 weight percent of $FeS_{2(total)}$. When a disulfide was not detected, it is reported as less than 5 weight percent of $FeS_{2(total)}$. Calibration standards for XRD (table 4) were prepared from mixtures of marcasite from Czechoslovakian hydrothermal deposits and pyrite from Climax, Colorado, which were each $\geq$95 weight percent FeS_2 as shown by XRD. The pyrite and marcasite were rinsed for

Table 4. Weight percent compositions and relative intensity ratios used in X-ray diffraction determination of synthetic FeS_2 phases. The intensity ratios are plotted in Figure 4.

Standard Number	Weight Percent Pyrite, P	Weight Percent Marcasite, M	Height Ratio: M(*211*)/P(*311*)
1	100	0	*.04
2	95	5	.06
3	90	10	.07
4	80	20	.11
5	70	30	.17
6	60	40	.33
7	50	50	.60
8	40	60	1.0
9	30	70	1.6
10	20	80	2.9
11	10	90	4.7
12	5	95	6.9
13	0	100	*8.0

*End-member values were obtained by extrapolation of data from standards 2-12.

30 minutes in 6M HCl (25° C) to remove Fe and S oxidation products, extracted with toluene to remove S°, powdered to <80 mesh to approximate the small FeS_2 grain size obtained in some experiments, and then mixed in the proportions shown in table 4. The ground standards were stored dry until needed and XRD indicated that the FeS_2 mixtures were not altered during storage.

A typical calibration curve generated from XRD of pyrite-marcasite standards is shown in figure 4. Known weight percent compositions are related to the measured ratio of the intensity of the marcasite (*211*) reflection to the pyrite (*311*) reflection. (These reflections correspond to peaks at 51.9° (2θ) for marcasite and 56.3° (2θ) for pyrite). Standards and pure sample disulfides were scanned using slower speeds (1/2° 2θ per minute) to obtain maximum diffraction intensities. Sample disulfide compositions were determined from calibration curves generated at the time of sample measurement. XRD calibration curves produced at different times using identical FeS_2 mixtures indicated that derived disulfide abundances have a precision of ±5 weight percent.

Mineral grain mount preparation

Reflected light microscopy of polished grain mounts was employed to examine mineralogical associations of pyrite and marcasite with one another and with other minerals, especially elemental sulfur. Grain mounts were prepared from unleached (raw) and 6M HCl-leached solids and examined under an oil immersion lens (X400). Mineral grains were mounted in epoxide cement and then sequentially polished with 300, 400, and 600 grit garnet paper. A non-aqueous lubricant was used for all polishing steps to inhibit oxidation of fine-grained disulfides. The mounts were cleaned between each polishing step by ultrasonication in the lubricant. This was followed by sequential polishing with diamond paste of 5, 3, and 1 µm, again with cleaning by ultrasonication between polishes. After a final 0.6 µm alumina polish and cleaning, the samples were viewed under reflected light.

Solution Analysis

Flame atomic absorption spectrophotometry

The chemical composition of reaction solutions was determined to characterize changes in solution chemistry that occurred during the experiment. For example, the amount of Fe not incorporated into solid phases is an indicator of the extent of reaction during disulfide formation, and the amount of solution Ca is a direct measure of the amount of $CaCO_3$ that had dissolved. The accumulated data was used with PHREEQE (Parkhurst et al., 1980) to chemically model the co-formation of marcasite and pyrite.

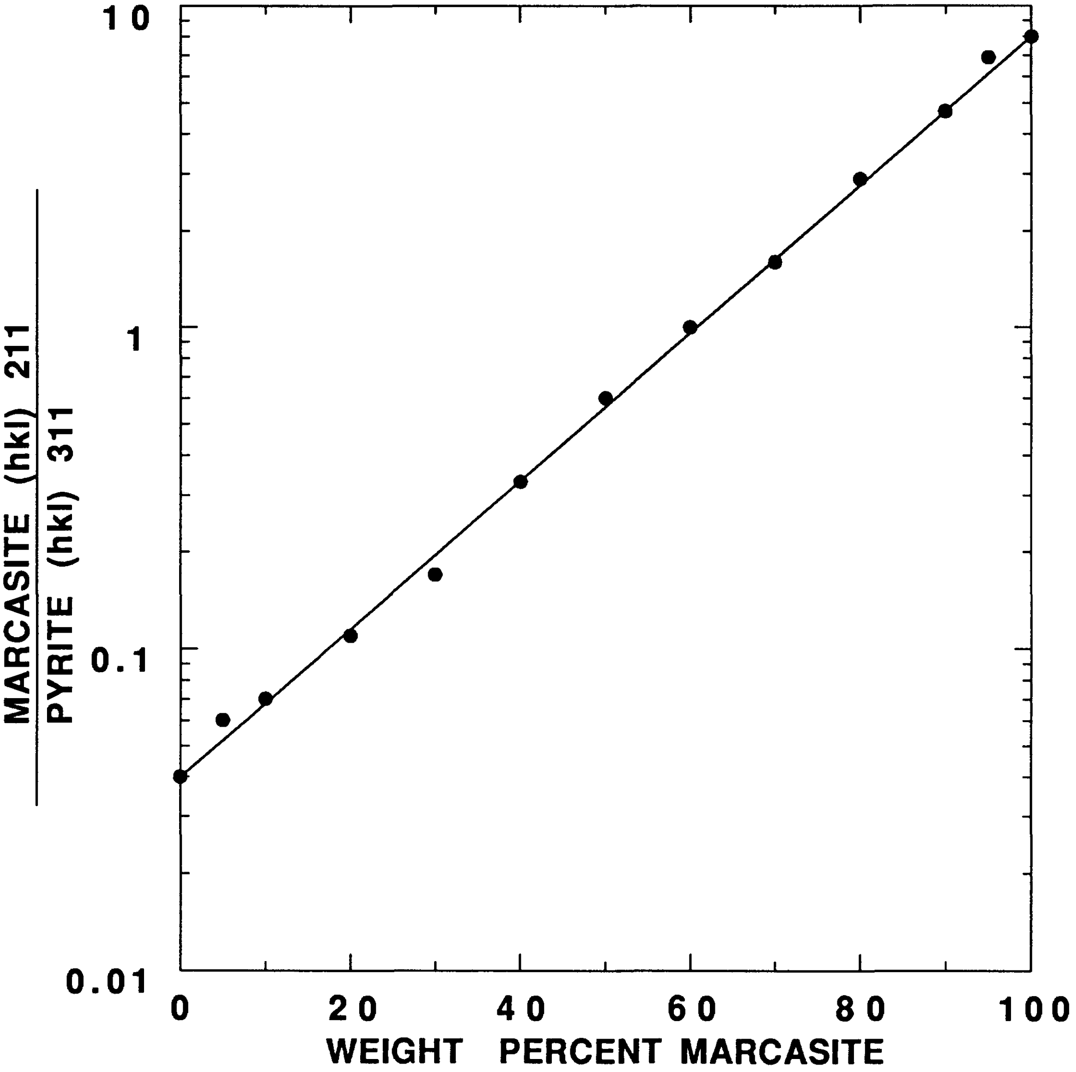

Figure 4. Typical X-ray diffraction calibration curve derived from known mixtures of pyrite and marcasite. Calibration line is based on the measured height ratio of the marcasite (211) reflection to the pyrite (311) reflection obtained from known weight percentage mixtures of marcasite and pyrite. Data used to construct this line is given in the last column of Table 4.

Iron analysis

The abundance of dissolved iron in solutions from the chloride and sulfate experiments is an indicator of the extent of reaction during FeS_2 formation. Thus, the amount of dissolved iron in the unreacted solutions, 6M HCl extracts, and final solutions was determined by FAAS. After dissolution of iron reagent in the unreacted solution, 1 mL was removed (replaced with 1 mL of distilled water) and diluted 1:2000 in 0.1M HCl for matrix-matching and to facilitate analysis within the lower working range of the AA to determine iron before reaction. Iron after reaction was determined employing similar dilution methodology. Iron from the 6M HCl leachates was determined after dilution in distilled water to approximately 0.1M HCl. Solution iron from the calcite series experiments was also determined in all unreacted and filtered (raw) reaction solutions, and filtrates from each 1M or 6M leach step. In some instances, greater dilutions (1:4000) were necessary, especially in experiments where large amounts of FeS and iron oxides were formed. The method was accurate to ±10 percent with a detection limit of 0.5 ppm Fe.

Calcium analysis

The amount of calcium in the final reaction solution of the calcite experiments was determined by FAAS to within ±10 percent and with a detection limit of 1 ppm Ca. If necessary, concentrated HCl (2-3 drops) was added to dissolve solid ferric oxide which had formed in some solutions several days after sampling. In all solutions, the acid concentration was adjusted to approximately 0.1N HCl prior to analysis. Dissolved Ca^{2+} in the raw filtrate may result, in part, from $CaCO_3$ dissolution caused by S° hydrolysis-generated acidity via reaction {1}. The protons generated may take part in calcite dissolution as illustrated by the following reaction

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad \{2\})$$

Sulfate analysis by $BaSO_4$ gravimetry

Solutions were analyzed for dissolved sulfate in all calcite series experiments and in those sulfate or chloride series experiments where only one of the sulfur reactants, either H_2S or S°, was added (tables 1-3). As noted earlier, an increase in sulfate could indicate that S° hydrolysis and oxidation to form additional sulfate, and(or) incorporation of S° into sulfide minerals (reaction {1}), may have occurred. While the formation of sulfate from reactions involving entrapped O_2 in the vessel walls cannot be discounted in experiments prior to number 40, the vessels were degassed for extended time periods for the calcite experiments. Sulfate was detected in all calcite series raw solutions and is probably a true product of reactions involving calcite. For the analysis, an aliquot of the reaction filtrate was acidified to pH ≤ 2 with nitric acid and heated at 90° C for 1 hour. $BaCl_2$ was then added to precipitate $BaSO_4$. The solid was digested at 90° C for an additional 6 hours, then filtered, thoroughly rinsed, dried, and weighed. Total sulfate was calculated from the weighed amount of solid $BaSO_4$.

RESULTS

Morphology and Texture of Solids

The locations, colors, and spatial relationships of the solid products were noted immediately upon opening the vessel and prior to filtration. Some solids formed at distinct places within the vessel and were identified with XRD as essentially pure phases. The most common solid products were thin layers of pyrite or marcasite that formed a smooth coating on the thermocouple and on the vessel walls. Macroscopically, the two FeS_2 phases could not be distinguished except that when pyrite was dominant (>80 weight percent), the solids were dark-green, and when marcasite was dominant (>70 weight percent), the solids exhibited a brassy silver color. Disulfide layers constituted the bulk of the solids in sulfate runs; these contained abundant marcasite. In addition to the thin marcasite layers on the vessel walls, partially-hollow marcasite spheres 1-3 mm in diameter were found floating on the solution surface or adhering to the layers. The marcasite spheres may have formed as coatings or replacements of viscous elemental sulfur spheres (described below). Evidence for this mode of formation was given by traces of S° visible inside some of the marcasite spheres. However, marcasite did not form a complete solid envelope around the S° (the marcasite spheres were about three-fourths completely formed) and the relationship of S° and marcasite may have been fortuitous. The S° may have been physically introduced into the marcasite sphere through mixing during the experiment or filtration. Pyrite layers and spheres were also produced in sulfate series experiments and resembled those of marcasite, including the presence of relict S° within spheres, an additional indication that reaction at the sulfur surface may be important in disulfide formation. In many instances, the sulfur appeared to grade into dark-colored disulfide. Other researchers have noted that the elemental sulfur surface may be a site of reaction during FeS_2 formation at lower temperatures (<85° C; Kribek, 1975; Berner, 1969).

Unreacted flowers of sulfur were present in experiments run at temperatures below 100° C. Three forms of S° were recognized from experiments run above 100° C - crystalline brown, viscous brown, and viscous yellow. The viscous forms were highly reflective liquids with a pearly luster, and elongate stringers of sulfur were attached to a central sulfur sphere. Upon cooling to below 100° C, the viscous forms produced hardened, brittle solids. The crystalline brown sulfur was found in most intermediate temperature experiments (100-150° C) while the two viscous forms were likely sulfur that had melted and polymerized. Some solutions containing viscous sulfur appeared lime-green or brown; this may have been due to the presence of polysulfides. In two cases, the viscous sulfur itself was lime-green (experiments 38A and 38B) and may have been due to polysulfides, coloration by the ferrous reagent, or perhaps both. Viscous sulfur was usually a product of higher temperature experiments of short duration (150-200° C; <24 hours) in which disulfide formation did not consume most of the sulfur. Hematite was restricted to a very thin layer between the vessel walls and the disulfide layer. The localization of hematite at this vessel wall-solution interface suggests that entrapped O_2 in the vessel walls produced the Fe_2O_3 layer through oxidation of the ferrous reagent. Magnetite, anhydrite, and gypsum that formed in the calcite series experiments, on the other hand, were found throughout and apparently not restricted to specific locations within the vessel.

Sulfate Series Subgroups

The sulfate series was divided into several subgroups based on the reaction variable(s) examined; these subgroups are briefly described here in conjunction with the experimental results. In the discussion that follows, the results of the experiments are examined primarily with respect to the influence of reaction time, temperature, and initial acid concentration on the yield of $FeS_{2(total)}$ (pyrite + marcasite) and weight percent of marcasite. Acid concentrations given are the initial acid concentrations before reaction and do not take into account proton generation or consumption which may have occurred during the experiment. Results are expressed as the weight percent of marcasite in recovered mixtures of marcasite and pyrite.

Heat-Cool subgroups: 19A-G, 20A-G, 27A-E, and 28A-FII

Four subgroups of experiments examined the formation of FeS_2 at 150° C and 200° C for varying and usually short (<24 hours) time periods. Experiments 19A-G (0.16 M H_2SO_4) and 20A-G (0.07M H_2SO_4) are denoted as H/C in table 1 (heat to temperature and cool). As soon as the desired temperature was reached, the vessel was immediately cooled in a compressed air stream; the compressed air cooling required <1/2 hour. Experiments 19A-G and 20A-G show that FeS_2 forms rapidly at temperatures above 150° C and not at some lower temperature during the heating stage. Only traces of disulfides formed for reaction times less than 3 hours (experiment 20-E). Longer reaction times at 150° C (experiments 27A-E, discussed below) produced higher yields of FeS_2, indicating that time is an important variable under these experimental conditions.

Results from the H/C experiments at 200° C (19F, G and 20F, G) showed that approximately 0.1 g of FeS_2 formed during the heating cycle. This amount was small compared to the yield of FeS_2 produced by reactions longer than 12 hours (1-2 g) at this temperature. The amount of FeS_2 formed remained relatively constant in reactions lasting more than 12 hours, indicating that the reaction was generally complete within this time period. Most experiments were therefore run for longer time periods (24 hours) at higher temperature (200° C) to obtain greater yields of disulfide.

Experiments 27A-E (150° C) and 28A-FII (200° C) examined the effect of reaction time at an acid concentration of 0.07M H_2SO_4. As the reaction time lengthened, the yield of $FeS_{2(total)}$ increased from a trace of FeS_2 in experiment 27A to almost 0.8 g in 27E. A gradual increase in the marcasite fraction was seen in the 27A-E subgroup with reaction times up to 25 hours; beyond 25 hours, the marcasite fraction appeared to remain nearly constant. Similar trends appear in the 28A-FII subgroup but are not as well-defined, and may have been due to undetected leakage of the solution past the decaying pressure release disc in some experiments.

Other subgroups

In experiments 22A-D, the influence of different H_2SO_4 concentrations with 10 times less iron reagent (0.75g = 0.018M Fe) than most other experiments was examined. Not unexpectedly, lower yields of $FeS_{2(total)}$ were produced compared to experiments with higher iron concentrations. As the initial H_2SO_4 concentration increased from 0.0006 (22-A) to 0.11M (22-D), the yield of $FeS_{2(total)}$ decreased from a maximum of approximately 0.3 g to essentially 0 g. The marcasite fraction was from 74 (22-A) to 92 (22-C) weight percent of the FeS_2, and marcasite was not detected in solids from the 0.11M H_2SO_4 experiment (22-D).

Experiments 33A-C were run over a range of both iron concentration (0.04 M Fe to 0.13 M Fe) and added elemental sulfur (0.19 g to 0.56 g). The lower initial abundances of these 2 reactants resulted in reduced yields of $FeS_{2(total)}$. The marcasite fraction was 68-86 weight percent, comparable to experiments run with "normal" amounts of Fe (0.18 M) and S° (0.75 g).

36A-D and 36-0-3 were run with 0.02M H_2SO_4 over a range of reaction times to test the effect of lower acid concentration on FeS_2 formation. These subgroups produced the highest yields of $FeS_{2(total)}$ of any sulfate experiments, but the marcasite fraction was lower, ranging from 28 to 61 weight percent; thus, the bulk of $FeS_{2(total)}$ was pyrite. Experiment 36-2, however, was anomalous in having a marcasite fraction of 94 weight percent. The results generally agree with the observed increase in the fraction of pyrite formed relative to marcasite as the initial acid concentration decreases.

Experiments 37A-D examined the reaction at different acid concentrations (0.005-0.07 M) in the absence of elemental sulfur. An interesting result was that the marcasite fraction was generally low (11-44 weight percent) compared to most other sulfate series experiments. These results suggest that elemental sulfur plays a key role in the formation of marcasite.

Experiments 38A-E and 39 were run with different H_2SO_4 concentrations and H_2S was not used as a reactant. The most noteworthy result from this subgroup is that highly pure marcasite ($\geq$89 weight percent) was formed in all but one instance. Experiment 38-A produced a very small yield of disulfide and so the fractions of marcasite and pyrite were unobtainable. The small yield was probably the result of the high initial acid concentration in this experiment.

FeS_2 Yield and Marcasite Fraction at 150° C

As mentioned earlier, iron disulfides did not form below 150° C. Generally, only the added elemental sulfur and minor FeS were present in the solid products from reactions at less than 150° C. Experiments 27A-27E showed that the yields of disulfides at 150° C increased as reaction time extended past 3 hours, although FeS_2 yields were still smaller than for similar experiments at 200° C. At 1 hour (experiment 27A), only a trace of FeS_2 formed and at 64 hours (experiment 27E), the FeS_2 yield increased to about 0.8 g. The marcasite fractions ranged from a trace to 74 weight percent for experiments 27A and 27E, respectively.

Experiments 28A through 28EII at 200° C were analogous to the 27A-E series. At 1 hour (experiment 28A), 0.01 g FeS_2 formed, and by 24 hours (experiment 28D), 1.76 g of FeS_2 formed, nearly four times the yield for 24 hours at 150° C. The marcasite fraction ranged from 45 to 64 weight percent of $FeS_{2(total)}$ for experiments 28A and 28D, respectively. Thus, the yield of $FeS_{2(total)}$ was greater at 200° C than at 150° C although the relative amount of marcasite was similar.

FeS_2 Yield and Marcasite Fraction at 200° C

Marcasite fraction vs molarity of H_2SO_4 or HCl

A major purpose of these experiments was to determine the conditions favoring formation of marcasite relative to pyrite. In the sulfate series, the weight percent of marcasite in recovered disulfides increased as the initial concentration of H_2SO_4 increased from 0.02 to 0.20 M as shown in figure 5. However, from 0.20-0.24 M H_2SO_4, the weight of $FeS_{2(total)}$ decreased from 1.45 g to 0.028 g, and the weight percent of marcasite dropped from 90-95 to <5. Marcasite was detected by XRD in samples from 0.20M and 0.22M H_2SO_4 experiments, but not in the experiment run at 0.24M H_2SO_4. This sharp break in the formation of marcasite and pyrite over similar ranges of increasing acidity has been observed by other researchers, for example, Allen and others (1912), Berner (1970), and Murowchick (1984).

In chloride series experiments, marcasite constituted 57-92 weight percent of $FeS_{2(total)}$, comparable to the weight fraction of marcasite in sulfate series experiments. However, maximum weight fractions of marcasite occur at lower concentrations of HCl (~0.01 M) than H_2SO_4 (0.02 M). The regular decrease in the weight fraction of marcasite as HCl

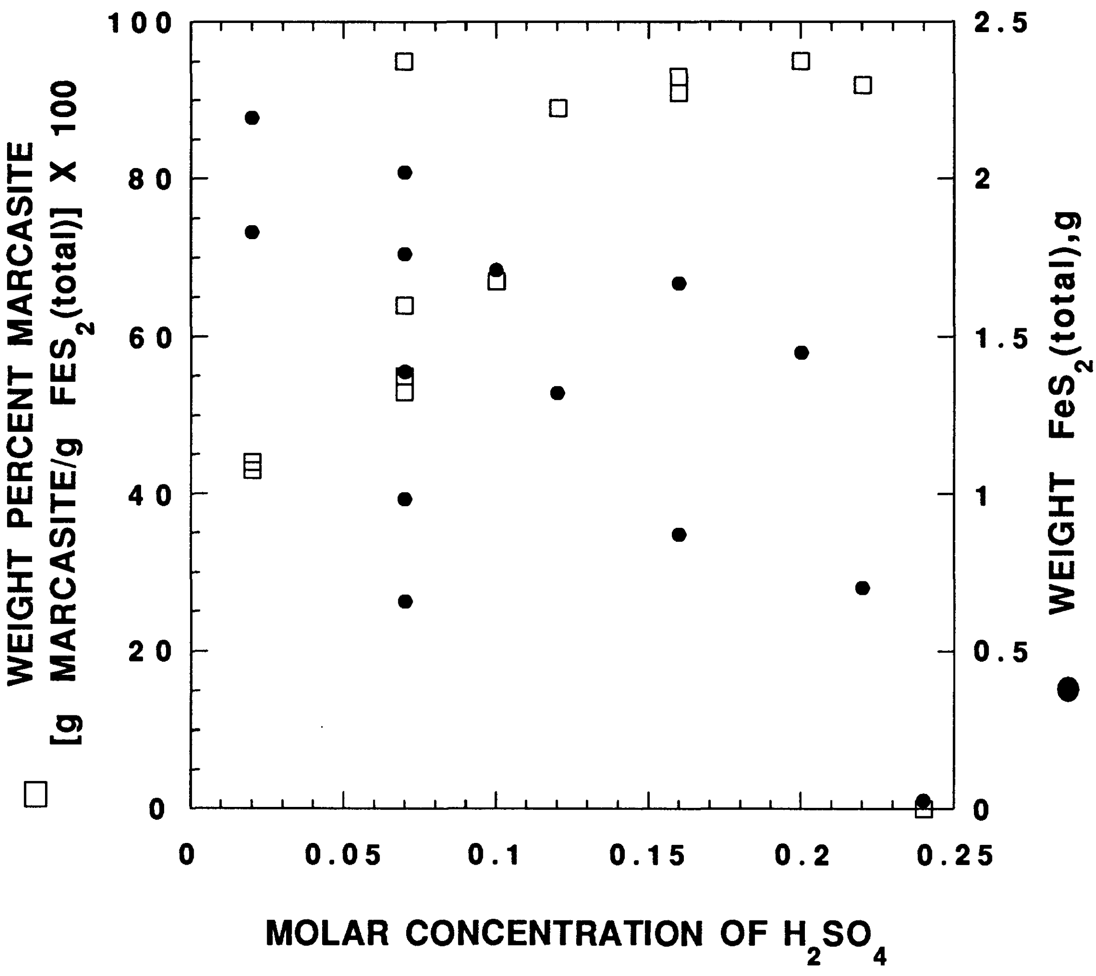

Figure 5. Weight of FeS_2(total) and weight percent of marcasite in FeS_2(total) plotted versus molarity of H_2SO_4.

molarity increases from 0.01 to 0.03 M is illustrated in figure 6.

FeS_2 yield and marcasite fraction in calcite series experiments

The presence of $CaCO_3$ diminishes the weight fraction of marcasite in the product disulfides. Qualitative pH measurement (litmus paper) showed that the pH immediately after reaction was ranged from 6 to 7 for all solutions. Unfortunately, without accurate pH values measured during reaction, it is difficult to identify pH changes that may have influenced disulfide formation. Nonetheless, marcasite was below the detection limit of XRD (<5 weight percent) in 6 calcite series experiments, and exceeded 50 weight percent of $FeS_{2(total)}$ in only 2 experiments (see table 3). In these 2 experiments, no residual solid $CaCO_3$ was detected; thus, sufficient proton generation apparently occurred to overcome neutralization by $CaCO_3$ and marcasite formation proceeded in the acid solution. In the 7 remaining experiments, marcasite was from 9 to 33 weight percent of $FeS_{2(total)}$. The weight fraction of marcasite in calcite series experiments decreased as the weight of residual $CaCO_3$ increased (figure 7). The points at zero residual calcite are from 5 sulfate series experiments in which H_2S was not added (38B-E and 39) and thus represent end member reactions without added $CaCO_3$.

SUMMARY

The formation of nearly pure marcasite or pyrite ($\geq$95 weight percent of $FeS_{2(total)}$) at 200° C occurred primarily in acid-sulfate and acid-chloride solutions. The weight fraction of marcasite began to decrease at >0.20 M H_2SO_4 and >0.01 M HCl. Marcasite exceeded 33 weight percent in only two calcite series experiments and pyrite was the dominant FeS_2 phase in other calcite series experiments. Calcite series experiments generally produced lower total amounts of disulfides, whereas in the sulfate and chloride experiments, $FeS_{2(total)}$ often made up 95 weight percent of total solids (with minor residual S°). The formation of marcasite and pyrite together was common in all experimental series, although one disulfide often predominated. Thus, the synthesis of FeS_2 at 150-200° C may produce pure or mixed FeS_2 phases, and minerals other than FeS_2 form in the presence of $CaCO_3$.

The synthesis and purification scheme outlined here may be useful for experimental work requiring highly pure marcasite or pyrite. The results illustrate that acid type and concentration are important controls on the formation of marcasite and pyrite at low pH. The presence of calcium carbonate may be important in controlling the amount and(or) type of FeS_2 that forms. The formation of minerals such as magnetite and anhydrite, which are often associated with sulfide ore deposits, may also warrant further investigation.

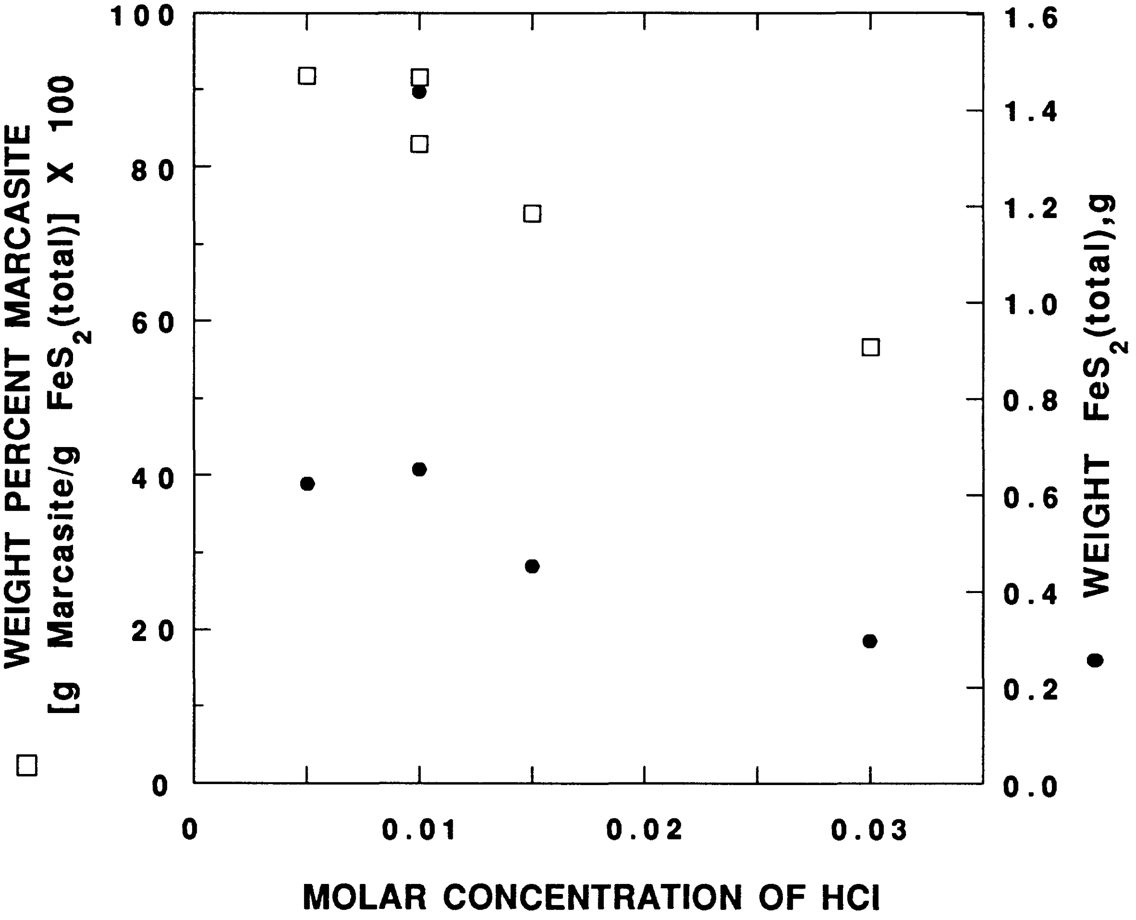

Figure 6. Weight of FeS_2(total) and weight percent of marcasite in FeS_2(total) plotted versus molarity of HCl.

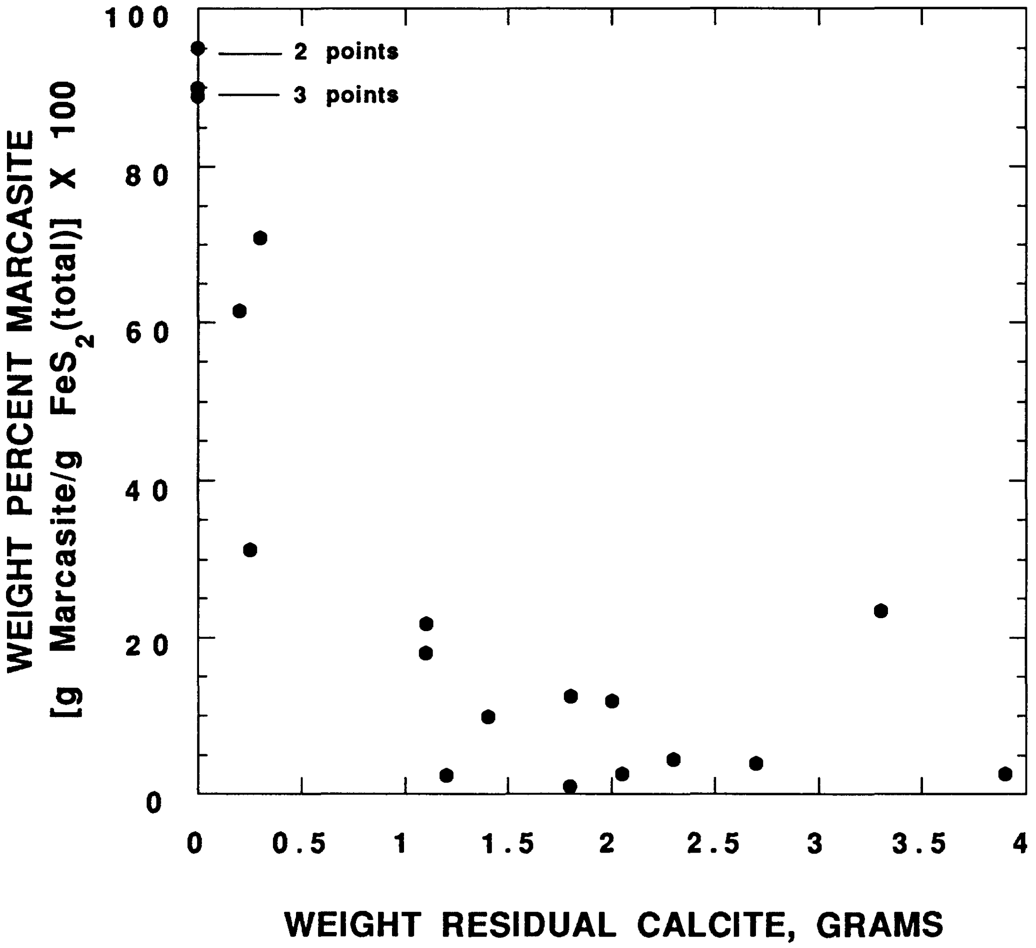

Figure 7. Weight percent of marcasite in FeS_2(total) plotted versus weight of residual calcite (grams).

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