SURFACE CONDITIONS OF THE ORGUEIL METEORITE PARENT BODY AS INDICATED BY MINERAL ASSOCIATIONS

by

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Abstract

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A study of the Orgueil meteorite shows that three main periods of mineral formation can be recognized: 1) an early stage with minerals like troilite, that are stable at several hundred degrees centigrade: 2) a middle stage with minerals like chlorite and limonite formed below 170°C and 3) a late stage with carbonates and sulphates, formed below 50°C. A physico-chemical analysis of the mineral-forming conditions indicates that oxidized phases like sulphate and limonite cannot be formed as a result of a local equilibrium but that an oxidizing substance must be brought into the system.

Volatiles like CO, CO_2 and H_2O may emanate from the interior of a meteorite parent body but none of these can oxidize troilite to limonite and sulphate. A possibility is that water at the surface of the parent body was dissociated by ultraviolet light to hydrogen and oxygen compounds, of which the lighter hydrogen escaped whereas at least some fraction of the oxygen or peroxides reacted with solid phases on the surface of the meteorite parent body.

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I. Introduction

The carbonaceous meteorites have lately attracted much interest. Particularly the "organic" compounds have been extensively analyzed because of the suggestion (Claus and Nagy, 1961) that part of this material may be of extraterrestrial biogenic origin. However, the characteristics of the inorganic compounds which constitute some 90 to 95 percent of these meteorites are still little known. This is due to the fact that carbonaceous chondrites mainly contain extremely fine-grained minerals, some of which are poorly crystallized and have varying chemical composition. Moreover, sample material is relatively hard to obtain, and the opacity of petrographic thin sections due to the presence of organic compounds renders microscopical observations difficult.

The mineral associations in carbonaceous chondrites have been studied recently be DuFresne and Anders (1962), Mason (1962), Nagy et al. (1963a) and Fredriksson and Keil (1964). DuFresne and Anders attempted to show, mainly by means of e-pH diagrams, that low temperature minerals in meteorites like Orgueil and Murray formed from high temperature minerals during an aqueous stage were close to equilibrium. Keil and Fredriksson on the other hand showed that Murray consists of at least two parts, which have been mechanically mixed together, one of high and one of low temperature origin.

In the present work the available data are summarized (sections 2 and 3), and used for a physico-chemical treatment to estimate the conditions that governed the formation of the minerals in one of the carbonaceous chondrites, the Orgueil meteorite. The relations derived give some indications of the surface conditions of the parent body. The material studied was obtained from the Swedish Museum of Natural History and from the "Nagy sample" (Nagy et al., 1964). In both cases it was ascertained that the samples had the original texture and did not contain gross contaminations (Anders et al., 1964).

2. Mineralogical composition of the Orgueil Meteorite

The Orgueil meteorite can be described as a bituminous clay with a clastic texture. This bituminous clay shows a breccia structure,(Figure 1), the fragments and the matrix having identical composition under the microscope and microprobe.

The major part of the meteorite consists of a lattice layer silicate constituting some 3/4 of the total material (Table 4c). A number of accessory minerals are listed in the same table. The meteorite is traversed by thin veins, mainly containing sulfates, which seem to be the last crystallized minerals. Mineralogical and paragenetical evidence given in sections 2-4 are summarized in Table 5. In the following the composition of each mineral is discussed, as well as the experimental methods for estimating the amounts present.

Chlorite The major phase has long been considered to be "like serpentine or chlorite" (Pisani, 1864). Mason (1962) preferred serpentine because of the low aluminum content. On the basis of x-ray analysis, Nagy et al. (1963a) concluded that the mineral probably was a chlorite; this conclusion is to some extent supported by the present results. In the present work the chemical composition of the groundmass was determined by electron microprobe x-ray analysis. The thin sections used for the analysis were moved at a rate of 8 micron/min. under the electron beam and the x-ray intensities for SiKα, MgKα, and FeKα, were integrated over periods of 20 sec. (Fredriksson and Keil, 1964). A similar procedure was followed for the elements Ni, S, and Al along the same tracks.

From several hundred microns of such tracks three parts each approximately 15 μ long were selected. Within these parts all six elements varied less than ±10% and these parts were considered representative for the predominant phase. Table 1 shows the composition of this phase in weight percent.

A partial analysis by Jarosewich (1965, see Table 2) shows that probably all of the sulphur in Table 1 is present as a water-soluble sulphate, mainly a magnesium sulphate. This is to be expected since the amount of sulphate in silicates commonly is low (Ricke, 1960). Probably the sulphate is present in a finely divided form or is absorbed on the layer lattice silicate. Calcium was not accurately determined, since its concentration is low compared with the other elements and most of it is present in other minerals. Further, since Ca is 8-coordinated it should not enter the chlorite structure to any large extent.

Provided that aluminum is mainly present in 6-coordinated positions and after the water-soluble quantities of magnesium and sulphate as found by Jarosewich (see Table 2) have been deducted the probe analysis can be written either,

$$(Mg, Fe^{2+}, Ni, Al)_{5.93}\ OH_{7.86}\ O_{0.14}\ Si_4\ O_{10}$$

or

$$(Mg, Fe^{3+}, Ni, Al)_{5.93}\ OH_{5.75}\ O_{2.25}\ Si_4\ O_{10}$$

the formulas representing the extreme cases. According to Table 2 it is evident that most iron in the chlorite is ferric, since much of the ferrous iron must be present in troilite and breunnerite.

Approximately 1 percent sodium is probably present (Figure 10), and this to some extent accounts for the deficiency in cations. Small amounts of potassium, chromium, and manganese are probably present (compare p. 17). Potassium and manganese have also been found in sulphates and carbonates (Nagy and Andersen, 1964).

The electron micrograph (Fig. 2) and the electron diffraction patterns from several grains (Fig. 3) also make it probable that the groundmass consists of a chlorite. Using MgO as a standard one of the pseudohexagonal patterns (Figure 3) gave the cell dimensions in Table 3, which compare well with data given by Kerridge (1964). In the same table unit cell dimensions of substances with a chemical composition similar to that of the major phase are given. Compared with this observed unit cell, ordinary chlorites (the nomenclature of Deer, Howie, and Zussman, 1962, and Brindley and Youell, 1953 is followed) have fairly large cell dimensions which increase with the iron content according to the formulas by Hey (1954) for $\underline{a}$, $\underline{b}$, and $\underline{c}$. The cell dimensions indicate that the mineral probably is a ferric chamosite in good agreement with Jarosewich's data. The broad undefined (001) reflection (Nagy et al., 1963) indicates a stacking disorder.

The quantity of chlorite in the meteorite has been estimated at about 75 volume percent according to microprobe traverses, areal estimates of microradiographs (Figure 5), electron probe scanning (Figure 7), and microscopic observations on five thin sections, about 5-10 microns thick. The values in Table 4c are based on the calculation discussed in sections 3 and 4.

Magnetite Fe_3O_4, is one of the phases in Orgueil that is easy to observe and isolate. X-ray micro-radiographs (the method is described by Fredriksson, 1958), Figures 5a and 5b, illustrate the distribution, relative amount and shape of the magnetite grains. It appears that the magnetite occurs in two forms: (a) as micron-sized, irregular grains, and (b) as spherical particles from a few microns to some 40 microns in diameter, several of them being hollow (Figure 6a and 6b). A few of the spherules have been analyzed with the microprobe, both in thin sections and as isolated grains. (The latter were kindly given to us by Dr. D. Parkin.) The spherules consist of an unusually pure magnetite. The Ni content is at most 100 ppm but probably less than 50 ppm, and the Mn content is only about 400 ppm. This is exceptional since most terrestrial magnetite (including our microprobe standard) contains 10 times more Ni, Mn and Cr. The high purity of the meteorite magnetite suggests that the magnetite spherules were formed at low temperatures, possibly by alteration of rounded aggregates of ferric hydroxide (see pages 7 and 9 below). Such recrystallization would explain, by shrinkage, why the spherules are hollow.

Some of the magnetite, however, is probably an early high temperature phase, perhaps even preceding the troilite. If the small irregular magnetite grains are of this type or are primordial condensates (Wood, 1963), they should contain considerably more trace elements, e.g. Ni than the spherules. Mason (1962) indicated that the magnetite in Orgueil has an unusual, large unit cell, and concluded that the composition might be close to trevorite ($NiFe_2O_4$). This appears to be in agreement with a high temperature origin for the major part of the "magnetite". Finally there seems to be a very late magnetite in the sulphate veins (Nagy, pers. com.).

Although this type of magnetite has not been found in the present work, it might be contemporaneous with the magnetite spherules.

It should be pointed out that the magnetite spherules morphologically resemble the cosmic spherules (Murray and Renard, 1891; Pettersson and Fredriksson, 1958; Castaing and Fredriksson, 1958; Hunter and Parkin, 1960; Thiel and Schmidt, 1961; and others) as well as volcanic magnetic spherules (Fredriksson and Martin, 1963). However, the Orgueil spherules contain less nickel than the cosmic spherules, and less manganese than the terrestrial ones and can consequently be distinguished by careful analysis. This offers an opportunity to ascertain the total influx to the Earth of carbonaceous meteorites of the Orgueil type by extracting and counting such spherules from slowly deposited deep-sea sediment (e.g. Petterson and Fredriksson, 1958) provided no authigenesis of similar spherules takes place in the deep-sea sediments. To distinguish between terrestrial spherules and cosmic spherules that are formed in the atmosphere by ablation of meteorites (Castaing and Fredriksson, 1958) and spherules from Group 1 carbonaceous chondrites (Wiik, 1956) they must all be analysed. Such an estimate seems most desirable, for it is probable that only few carbonaceous meteorites survive the passage through the atmosphere and those which do are hard to retrieve, whereas their resistant magnetite spherules mostly would survive. If the suggestion that some material with a composition close to that of Orgueil is the parent material for most meteorites is accepted (Mason, 1960; Ringwood, 1961; Fredriksson, 1963) there is good reason to believe that the number of carbonaceous meteorites entering the atmosphere is much higher than recovered falls indicate, at least at the present time.

The abundance of magnetite in Orgueil can be estimated from x-ray micro-radiographs (e.g. Figure 5) at approximately 4 volume percent. This agrees well with the calculated value in Table 4c, but is almost an order of magnitude lower than the estimate by DuFresne and Anders (1962, p. 1091; and Anders (1964, p. 630). If these values were correct no iron would be left for the chlorite, breunnerite and troilite (compare section 3 below). In 1864 Cloetz and Pisani found a content of 20.63 and 15.77 weight % respectively of magnetite, determined as insoluble in HCl, but these values were shown to be too high by Cohen (1894).

<u>Troilite</u> FeS (Fitch, et al, 1962) occurs largely as crystals from a few microns to a few hundred microns in diameter (Figures 4, 5, and 7). The habit suggests a hexagonal symmetry which indicates that the mineral probably is troilite. The monoclinic modification of FeS, smythite (Erd, et al, 1957) has also a hexagonal habit, but since smythite is rare and never has been observed in meteorites it seems most probable that the FeS-phase in Orgueil corresponds to troilite. To verify this an x-ray powder-pattern was made; several of the strong troilite lines could be found whereas none of the strongest smythite lines were present. Microprobe analysis of a number of grains indicate that 1.3 to 1.6 percent Ni substitutes for Fe. As shown in Figures 4 and 7, the troilite is frequently altered to ferric hydroxide, FeOOH, with some Ni and Cl (Nagy, et al, 1963b). Some brownish, highly refractive hexagonal particles which have been described as "organized elements" may also be alteration products of troilite (see further p. 12). Corroded troilite crystals are frequently associated with native sulphur, Figure 4.

The micro-radiographs, Figure 5<u>a</u> and 5<u>b</u>, as well as x-ray diffraction data indicate that troilite is less abundant than magnetite (i.e. 2 percent).

Sulphur S, occurs in native form (DuFresne and Anders, 1962). Figure 4 shows a few sulphur globules. They were first found in the magnetic fraction (size 44-88 microns) of a powdered sample since they to a large extent are associated with corroded crystals of magnetic troilite. It seems clear (Figure 4) that the troilite is an earlier mineral than the free sulphur. Some of the "globules" show crystal faces. They can be found in practically any untreated, newly broken up part of Orgueil. This contradicts the hypothesis that this type of sulphur globules may be an artifact produced by various sample treatments (Fitch, et al, 1962). Microscopic observation suggests that the crystals are orthorhombic. A chemical analysis of the meteorite by G. Jarosewich, Table 2, showed the presence of 1.6% free sulphur which is in good agreement with analyses by Anders, et al (pers. comm.). This value is considerably higher than the estimate made from direct microscopic observations, indicating that some of the sulphur may be very fine-grained.

Ferric hydroxide has been described by Nagy, et al,(1963b) under the name limonite, occurring in some of the particles described as organized elements. Since the real identity of the ferric hydroxide is unknown the name limonite ($FeOOH \cdot nH_2O$) will be retained here in accordance with the recommendation of Palache, Berman and Frondel (1944). The limonite contains minor amounts of nickel and chlorine. Figures 4 and 7 show that it is an alteration product of troilite, although in some cases it appears to be redeposited in available pores, for instance in the bubbles of "organized elements". The limonite is older than the veins and probably also older than the previously mentioned magnetite spherules, p. 6 . Since the chlorite contains ferric iron it is possible that limonite and chlorite were formed simultaneously. Dr. B. Mason (pers. comm.) has suggested that the limonite might have formed by terrestrial oxidation, e. g., from lawrencite $(Fe,Ni)Cl_2$, or troilite $(Fe,Ni)S$. This appears unlikely because of the frequent association with "organized" elements, and because the magnetite spherules discussed on page 6 seem to be recrystallized limonite.

It has been shown that the compound FeOOH may incorporate Cl ions (Chow, 1964). The Cl content (up to 3 percent) of the Orgueil limonite indicates that the troilite was altered in an aqueous environment containing chlorine. A possibility that gaseous Cl_2 was in part responsible for this oxidation cennot be disregarded and as will be shown in section 5 some "external" sources of oxidizer seem necessary.

Direct observations of the quantities of limonite present are difficult to make; but it is only a minor constituent, probably occupying less than one volume percent of the meteorite.

<u>Breunnerite and dolomite</u> Breunnerite, $(Fe,Mg)CO_3$, was first discovered in Orgueil by Pisani (1864). A microprobe analysis by Nagy and Anderson (1964) showed 20 percent Mg and 12 percent Fe. According to microscopic observations some five volume percent of the meteorite is made up of strongly birefringent minerals presumably identical with the carbonates breunnerite, and dolomite. Dolomite, $CaMg\ (CO_3)_2$ has been found in Orgueil by DuFresne and Anders (1962), but has not been observed by the present authors or by Nagy and Andersen (1964). The abundance is not easily ascertained. According to the calculations in section 3 dolomite may be completely missing and at most be present only in small amounts; otherwise, considerably

less magnesium and calcium would be available for chlorite, epsomite, breunnerite and gypsum and more sodium sulphate would form (see section 3). The carbonates are not found in veins but may nevertheless be formed late since they commonly are fresh and well crystallized.

Gypsum $CaSO_4 \cdot 2H_2O$, is present as small individual grains according to Nagy and Andersen (1964). Compared with the theoretical formula for anhydrite, their probe analysis shows a deficiency of Ca and S which may be interpreted as indicating that the mineral is indeed gypsum, $CaSO_4 \cdot 2H_2O$ and not anhydrite, $CaSO_4$. It is not unlikely that this is the original form and if so it was probably formed below 50°C (Posnjak, 1938, 1940). The mineral seems to be present only in minute amounts, less than 1 volume percent, but since it is difficult to identify microscopically, it is not easy to estimate its abundance.

Magnesium sulphate $MgSO_4 \cdot nH_2O$, and a sodium-containing sulphate have been observed in the veins (Figure 9). The magnesium sulphate has been definitely identified (Cohen, 1894; DuFresne and Anders, 1962) but it is difficult to ascertain how much water of crystallization was present originally. The presence of a sodium sulphate has been inferred from mineralogical studies and analysis of water extracts of Orgueil sample, (DuFresne and Anders, 1962) showing that sodium may well be present in some double salt, e.g. bloedite, $Na_2\ Mg(SO_4) \cdot 4H_2O$. Figure 9 illustrates the distribution of Na^{23}, Mg^{24}, Mg^{25}, and Si^{28} in the veins. It seems that the sodium-containing salt crystallized before the magnesium sulphate, but it might also have formed in late cracks since many sodium salts are very soluble. The amount of sulphates has been estimated as high as 17 percent (DuFresne and Anders, 1962), and indeed, exposed surfaces of certain samples (e.g. the main mass in Paris) show an abundant network of sulphate veins. The present work on thin sections indicates that such veins are less abundant than the carbonates, which is in agreement with observations by Nagy (personal communication). Sulphates in veins are estimated at 2 to 3% by volume; while the total amount of water soluble $MgSO_4 \cdot 7H_2O$ should be about 13.1 weight percent according to analysis by E. Jarosewich (see Table 2). This value is in good agreement with data by DuFresne and Anders (1962) and Anders,(pers. comm). Consequently it seems reasonable to assume that the sulphur found in the chlorite analyses in Table 1 is present as finely divided or absorbed sulphates, mostly of magnesium but also of some other cations e.g. iron, nickel, calcium and sodium.

Calcium phosphate was described in Orgueil by Nagy and Anderson (1964), and was tentatively identified as merrillite, $Na_2Ca_3(PO_4)_2O$, since the measured absolute mass concentrations of calcium and phosphorus are a little too low to suggest whitlochite, $\beta Ca_3(PO_4)_2$. However, sodium was not analyzed for (op. cit.) and the mineral may consequently be whitlockite, which is a common phosphate in many meteorites (Fuchs, 1962). No direct estimates of its abundance exist, but if all available phosphorus is ascribed to this mineral, a maximum of 0.8 volume percent can be calculated (see Table 4c). This amount does not influence the sodium or calcium balance significantly.

Brucite or Periclase $Mg(OH)_2$,MgO. A single 10μ cube-shaped grain of a mineral with a high Mg-content was found with the microprobe, (Figure 10). Subsequent analysis showed 50 percent Mg and approximately 1 percent Fe and 1 percent Si. The Mg content is too high for any likely compound other than periclase, MgO, or brucite, $Mg(OH)_2$. Theoretically brucite has 41 percent Mg and the high value of the present analysis may be explained if it is assumed that the vacuum in the probe and the heat from the electron beam boiled off water from brucite (see Table 6b). Probably also some excitation of the surrounding chlorite took place. This assumption is supported by the observed amounts of silicon. Periclase is not stable in the aqueous environment which seems necessary to explain the late vein minerals, p. 19 in Orgueil and this fact also supports the assumption that the mineral indeed is brucite, $Mg(OH)_2$.

Olivine $(Mg, Fe)_2 SiO_4$, has not been found with certainty. One 40μ large grain analysed with the microprobe showed Mg, Fe, and Si contents corresponding to an olivine with 95 percent forsterite. The crystal was lost and the identification could not be confirmed. J. F. Kerridge (1964) has inferred from electron diffraction data that Orgueil contains micron sized grains of olivine. It is however, difficult to understand how olivine, particularly in small grains, could survive in the aqueous environment in which the last-formed Orgueil minerals originated.

Several workers (e.g. Urey, 1957 and DuFresne and Anders, 1962) have suggested that the Orgueil was formed by alteration of some material of chondritic composition. During informal discussions some petrographers (e.g. Griffith in La Jolla, 1964) have suggested that some fragments like that in Figure 1 may be pseudomorphs after olivines or pyroxenes. Probe analyses showed that the fragment in Figure 1 has basically the same composition as the main mass except for a slight increase in nickel and sulphur. Consequently this particular fragment is apparently not an alteration product of a meteoritic olivine since these have generally extremely low nickel content. (Compare the discussion of the Murray carbonaceous chondrite by Fredriksson and Keil, 1964). It should be pointed out however, that the presence of a few olivine pseudomorphs would not contradict the tuffaceous character. On the other hand, if fresh olivine is still present it is almost necessary to assume that Orgueil is a mechanical mixture of high and low temperature phases similar to Murray (Fredriksson and Keil, 1964) and that fine grained olivine would have to be emplaced at a very late stage.

Carbonaceous compounds and organized elements No efforts have been made to identify any of the organic compounds. Some preliminary electron microprobe analyses by C. Andersen[1)] have indicated the presence of rounded aggregates, 10 to 30 microns in diameter, enriched in carbon, perhaps up to 30%. No direct correlation with any organized elements could be established. The possibility exists that these aggregates contain graphite because this mineral has been observed in Ivuna (Vdovykin, 1964). This work is presently being extended.

The results of some electron microprobe work reported by Nagy, et al, (1963b) has been confirmed with respect to the rounded aggregates of limonite coated with what appears to be a thin film of organic material. One of us (K.F.)has repeatedly in discussions offered the explanation that these "plastic shells" were formed by evaporation and recondensation of organic material on the walls of bubbles created by vapors. Subsequently limonite was deposited in voids after some low-boiling organic compounds. Alternatively organic material could be adsorbed on the surface of the limonite aggregates. It will be shown that the primitive material which ultimately became Orgueil must have been exposed to at least several hundred degrees centigrade, e.g. for the formation of euhedral troilite crystals, consequently a distillation

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of organic compounds present in the accumulation of primitive matter appears likely.

It is now obvious that the organized elements, type V, (Claus and Nagy, 1961, or Staplin, 1962) Sexangulatus Celestites mainly are altered troilite crystals (see Figures 7 and 11, p. 7). Mueller (1962) and Anders and Fitch (1963a), reached the same conclusion. The later suggestion by Fitch and Anders (1963b) that the type V organized elements are deformed pollens is, like the proposition of extraterrestrial fossils (Claus and Nagy, 1961), based entirely on a morphological argument.

3. Quantitative relations

In section 2 and Table 4c some figures for the quantities present of some minerals have been given. They have been derived by means of volumetric estimates from electron micrographs and microscopical observations and from the complete and partial chemical analyses of Orgueil I (Wiik, 1956; Jarosewich, Table 2) and of various minerals. An analysis of Orgueil II by Wiik (in Mason, 1962) showed virtually the same quantities of the various elements.

In these petro-chemical calculations some arbitrariness is necessarily involved. The following steps were followed in the calculation:

1) The analyses by Wiik (1956) and Jarosewich (see Table 2) were recalculated to an ignition loss free basis, assuming that both samples had the same amount of ignition loss. The number of moles available per 1000 g of this ignition loss free matter are given in Table 4a. The number of moles of native sulphur, S, water soluble sulphate, SO_4^{2-}, and magnesium, Mg^{2+}, are given in Table 4b. The figures in Tables 4a and 4b are more accurate than

is warranted by the chemical analyses but have been used in order not to introduce calculation errors.

2) The amount of native sulphur is then found to be 0.542 moles, S according to Table 4b.

3) From 2) and the quantities of sulphates* in Table 4b it is found that the amount of FeS can at most be 0.517 moles.

4) All phosphorus is used to form 0.021 moles merrillite of the composition $Na_2Ca_3(PO_4)_2O$.

5) All silicon is used to form chlorite (the composition is given in Table 1 and with the formula given on p. 4). This process also consumes all nickel.

6) All water soluble magnesium is used to form 0.559 moles magnesium sulphate of the composition $MgSO_4$.

7) All remaining magnesium and some iron form 0.314 moles breunnerite of the composition $Mg_{0.8}Fe_{0.2}CO_3$.

8) All remaining calcium forms 0.169 moles gypsum of the composition $CaSO_4 \cdot 2H_2O$.

9) All remaining sulphate forms 0.043 moles sodium sulphate of the composition Na_2SO_4.

10) All remaining iron forms 0.260 moles magnetite, Fe_3O_4 and 0.051 moles limonite, FeOOH. (There is no way to find these abundances from chemical data, but microprobe analyses approximately suggest their relative quantities.)

11) All remaining carbon forms 2.441 moles graphite**, C.

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* It is possible that the content of SO_4^{2-} in the meteorite is larger than Jarosewich found since some sulphates like gypsum are not very soluble.

** Vdovykin (1964) found graphite in Ivuna but whether it exists in Orgueil is not known.

12) After step 1-11 there remains (except oxygen and hydrogen)

element	moles
Na	0.127
K	0.016
Cr	0.051
Co	0.009
Al	0.065
Ti	0.009
Mn	0.029

which make up only 1.05% of ignition loss free material. Part of these metals (particularly sodium) are probably present in the chlorite which has a slight deficiency in metal ions (see p. 4). Some manganese and potassium is probably present in carbonates and sulphates (Nagy and Anderson, 1964).

4. Temperature and pressure conditions during the formation of the minerals.

The pressures and temperatures that controlled the formation of the minerals in Orgueil can be estimated by the following relations.

There are hexagonal, tetragonal and monoclinic modifications with approximately the composition FeS. The hexagonal form is stable from 743°C down to at least 325°C (Arnold, 1962) whereas the monoclinic form is unstable above 265°C (Moh and Kullerud, 1964). This indicates that the FeS-phase in Orgueil was formed above 265°C, but an exact minimum temperature is difficult to ascertain, since the stability field for the intermediate FeS form is unknown (op. cit.). Since Orgueil is water-rich it can be expected that a high water pressure will change the stability relations. Studies of the system Fe-S-H_2O indicate that FeS·nH_2O, hydrotroilite, may be stable at 100°C, which also indicates that the troilite formed at high temperatures (Moh and Kullerud, 1964).

Fe_3O_4 can be stable from very high temperatures, the melting point being 1591°C down to low temperatures (see Figures 15 a-b and 16 a-b) but the extent of the stability region depends on the partial pressures of oxygen, carbon dioxide and hydrogen sulphide.

Fe_3O_4 and FeS are stable together at least from 675°C (Kullerud, 1957) down to 325°C. Between 675 and 560°C (see Figure 12) FeS and Fe_3O_4 are stable together with either FeO or FeS_2 but not with Fe, Fe_2O_3 or S. Below 560°C (see Figure 13) FeS and Fe_3O_4 are stable together with either Fe or FeS_2 but not with Fe_2O_3 or S. It therefore seems evident that troilite and some of the magnetite in Orgueil represent an early association (see p. 6) that is not in equilibrium with native sulphur or limonite in the groundmass.

The stability conditions of chlorite are little known. According to Nelson and Roy (1958) 14Å chlorites may alter to 7Å chlorites when the temperature sinks below 350-500°C. The broad diffuse (001) peak and the absence of a well formed 14Å peak in the x-ray diffraction of the Orgueil chlorite (Nagy, et al, 1963a) indicates a stacking disorder in the structure. This suggests that the chlorite was formed at low temperature. It is probable that the iron content of the Orgueil chlorite will change these relations somewhat, since the phase diagrams by Nelson and Roy (1958) refer to iron-free chlorites.

Limonite probably was formed at low temperatures since goethite decomposes above 170°C at 900 bars (Schmalz, 1958). Limonite and native sulphur are clearly later than troilite (see Figure 4 and 7). The period of formation of the chlorite is uncertain but probably it acquired its present appearance about the same time as limonite was formed since both indicate an aqueous environment rich in ferric iron.

The presence of gypsum in the veins indicates that they were formed at temperatures below 100°C, probably in the range 0-42°C according to the results by Posnjak (1938, 1940). MacDonald (1953) showed that gypsum will precipitate out of sea water at all temperatures below 34°C (at one atmosphere) if the deposition is an equilibrium process. He further showed that variations in the pressure only have small effects; thus a pressure of 100 bars only raises this temperature to 35°C. Both Posnjak and MacDonald showed that at these low temperatures gypsum and not anhydrite was the stable form even in salt solutions 4.8 times more saline than sea water. It cannot be denied, however, that anhydrite might have been the primary mineral in Orgueil and that gypsum was formed by hydration during sample preparation or some other time after the fall.

The low temperature of formation and their occurrence in the veins indicates that the sulphates are among the latest formed minerals in Orgueil. The period of formation for the carbonates is less evident but their fresh appearance makes it highly probable that they also belong to the latest formed minerals in Orgueil.

No geologic manometer is present so far as we presently know. The brecciation of the meteorite before the formation of the veins indicates that the lithostatic pressure was not very high when the minerals in Stages II and III (see Table 5) were formed.

Table 5 summarizes the mineralogical and paragenetical evidence given in sections 2-4.

5. Stability conditions and the formation of the minerals

The natural approach would be to study the formation of the minerals in a chronological order but this is difficult to do without any preconceived idea of the parent material for Orgueil. It is possible, however to start with a study of the late minerals that were formed during Stage III (see Table 5). Once possible stability conditions for these are established their formation is easier to explain. This study shows that the veins most probably were formed in an open system, perhaps with free oxygen or peroxide as oxidizer. The tuffaceous structure and the presence of hydrous phases in the Orgueil meteorite indicates that the minerals may have been formed at the surface of a meteorite parent body.

To analyse the mineral forming conditions DuFresne and Anders (1962) and Nagy, et al, (1963a) used <u>e</u>-pH diagrams*. Like acid-base* and redox diagrams* they show the stability relations between various chemical species, but they fail to indicate in what quantities the substances take part in the reactions (Boström, 1965). Further the sizes of various stability areas for different compounds in an <u>e</u>-pH diagram, for example, depends on the activities of various chemical species in the solution. For this reason the order of magnitude of these activities must be known before diagrams can be constructed for the discussion below. The notation that will be used in the following is given in the appendix.

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* The reader is assumed to be familiar with the construction and use of such diagrams. They are extensively discussed elsewhere, e.g. Hägg (1940), Delahay, Pourbaix and van Rysselberghe (1950), Sillén (1952, 1959) and Boström, (1965).

The activities can be found in different ways. If the association is quantitatively very small compared with the solution with which it is in contact, it would be justified to assume that the composition of the solution changes little during the reactions so that consumption and production of various ions such as H^+ and OH^- can be disregarded (Boström, 1965). Another solution is possible for closed systems where we know how much has been consumed and produced of various species. It is then sometimes possible to find the activity distribution in the solution (op. cit.).

These approaches cannot be used in the present case since there is no evidence to justify the first approach, and there are no safe indications of the quantitative relations before the vein-forming reactions started. However, at equilibrium with a solution all solid phases must have their solubility products satisfied, and electroneutrality must hold for the solution. By means of these relations the activities can be calculated and e-pH diagrams can be drawn, after which it is possible to analyze the mineral-forming conditions. The physico-chemical constants are given in Tables 6a-6c. The variation in the stability constants between 0° and 42°C is small and we can therefore with good approximation use data for 25°C and 1 atm. for the main part of the discussion. How the constants are calculated is described in the appendix, p. 35.

From the descriptions above it seems natural to test whether epsomite, gypsum, breunnerite and dolomite can be stable together. The stability relations between the three first mentioned minerals will be studied first.

It may be objected that the degree of hydration is unknown in the sulphates and that some hydration took place after the fall of the meteorite.

However, if the minerals were formed at low temperatures in an aqueous environment, the sulphates probably would be precipitated in hydrated form.

For the late minerals the following formulas will be used.

epsomite	$MgSO_4 \cdot 7H_2O$
gypsum	$CaSO_4 \cdot 2H_2O$
breunnerite	$Mg_{0.8}Fe_{0.2}CO_3$
dolomite	$CaMg(CO_3)_2$

In the aqueous solution electroneutrality must hold, that is:

$$2(Mg^{2+}) + 2(Fe^{2+}) + 2(Ca^{2+}) + (H^+) = 2(SO_4^{2-}) + 2(CO_3^{2-}) + (OH^-) + (HSO_4^-) + (HCO_3^-)$$

Further, from the assumption that breunnerite behaves as an ideal solid solution and from the activity products in Table 4 and by setting $(Fe^{2+}) = \underline{x}$ we get*:

$$(Mg^{2+}) = 4\underline{x}$$

$$(CO_3^{2-}) = \frac{3.2 \times 10^{-9}}{5\underline{x}}$$

$$(SO_4^{2-}) = \frac{4.2 \times 10^{-5}}{4\underline{x}}$$

If brucite should also be in equilibrium with the solution we have the additional condition:

$$(OH^-) = \sqrt{\frac{8.9 \times 10^{-12}}{4\underline{x}}} = \frac{4.72 \times 10^{-6}}{\sqrt{\underline{x}}}$$

---

* It can be objected that $(Mg, Fe)CO_3$ is not an ideal solution. However, even if the ratio $\frac{(Mg^{2+})}{(Fe^{2+})}$ is varied between 1 and 10 the calculations below are little affected.

From the relations above and the fact that (Table 4b)

$$\frac{(CO_3^{2-})\ (H^+)}{(HCO_3^-)} = 4.69 \times 10^{-11}$$

we further derive:

$$(HCO_3^-) = \frac{2.88 \times 10^{-8}}{\underline{x}}$$

and:

$$(Ca^{2+}) = \frac{2.4 \times 10^{-5}}{4.2 \times 10^{-5}} \times 4\underline{x} = 2.28\underline{x}$$

(HSO_4^-) and (H^+) can be neglected (see Figure 14) since there are no indications of strongly acid conditions under which limonite or carbonates would be unstable.

Substituting the activities in the electroneutrality condition with the expressions derived for the various activities we get:

$$\underline{x}^2 - 3.26 \times 10^{-7}\ \underline{x} = 1.44 \times 10^{-6}$$

$$\underline{x} = 1.21 \times 10^{-3}$$

The calculated activities are given in Table 7 for various pH values in the solution. Column a gives the activities in the solution when pH and (Mg^{2+}) are high enough to form brucite. Columns b-d give the activities in other solutions which fulfill the relations deduced above except that brucite is not stable. A check shows that electroneutrality holds for all these solutions and that breunnerite, gypsum, epsomite, and dolomite all have their activity products satisfied.

These calculations do not consider the valence changes in the sulphur or iron compounds. Figures 16a-b show in what areas of the system Fe-H_2O-H_2CO_3 the derived relations are valid. (Since the activity of $MgCO_3$ in breunnerite is larger than the activity of $FeCO_3$ the stability field for breunnerite should be larger than that for $FeCO_3$ in Figures 16a-b, but this difference is so small that it can be neglected for this study.) The shaded area indicates where the carbonates and sulphates can be stable together. By combining the calculated activities with the information in Figures 16a-b we find that at 25°C the carbonates can only be at equilibrium with substantial quantities of sulphate when $(H_2CO_{3\ tot}) > 10^{-3}$. High temperature requires even larger carbonic acid activities. When $(H_2CO_{3\ tot})$ is about 10^{-2} at 25°C this condition is fulfilled between pH = 5-7. Of interest is also that under these condition magnetite is a stable phase.

Under these neutral or slightly acid conditions breunnerite, gypsum, epsomite, dolomite and magnetite can be stable together. The activities in Table 5 further show that compounds such as calcite and melanterite are not stable under such conditions. It is an interesting fact that neither of these minerals have been observed in Orgueil or carbonaceous meteorites in general. The calculations further show that the carbonates and sulphates discussed above are not stable with brucite.

The presence of sodium sulphate has not been considered above, since the total amount of sodium sulphate present seems to be very small as indicated on page 10.

This study does not prove that the vein minerals were formed simultaneously with the carbonates but it is possible and seems very likely. Figures 15, 16, 17, and the data in Table 4 further show that the association of brucite, troilite, native sulphur, sulphates and carbonates is unstable.

Thus for instance brucite only should be stable at pH = 10.1, a value that will be only slightly decreased by the Fe^{2+} content of the solution. It is therefore obvious that the conditions in Orgueil do not represent equilibrium between all the coexisting phases, which is also clearly illustrated by Figure 7 and by the stability data given in section 4.

The seemingly simplest explanation of how the low-temperature minerals were formed would be to assume that they were formed as a result of reactions between phases in the present groundmass.

Redox processes between limonite, troilite and native sulphur are possible, (Figures 15 and 17) forming SO_4^{2-}, Fe^{2+} and Fe_3O_4. The following equations for the limiting cases can be written (the figures below the formulas indicate the number of moles consumed or formed during the reaction, assuming that 0.77 moles SO_4^{2-} is formed by the process);

$$(1)\quad \begin{array}{llllll} 26\ \mathrm{FeOOH} + & \mathrm{FeS} + \longrightarrow & \mathrm{SO_4^{2-}} + & 9\mathrm{Fe_3O_4} + & 12\mathrm{H_2O} + & 2\mathrm{H^+} \\ 20.02 & 0.77 & 0.77 & 6.93 & 9.24 & 1.54 \end{array}$$

$$(2)\quad \begin{array}{llllll} 18\ \mathrm{FeOOH} + & \mathrm{S} \quad + \longrightarrow & 6\mathrm{Fe_3O_4} + & \mathrm{SO_4^{2-}} + & 8\mathrm{H_2O} + & 2\mathrm{H^+} \\ 13.86 & 0.77 & 4.62 & 0.77 & 6.16 & 1.54 \end{array}$$

$$(3)\quad \begin{array}{llllll} 8\ \mathrm{FeOOH} + & \mathrm{FeS} + & 4\mathrm{H_2O} \longrightarrow & 9\mathrm{Fe^{2+}} + & \mathrm{SO_4^{2-}} + & 16\ \mathrm{OH^-} \\ 6.16 & 0.77 & 3.08 & 6.93 & 0.77 & 12.32 \end{array}$$

$$(4)\quad \begin{array}{llllll} 6\ \mathrm{FeOOH} + & \mathrm{S} + & 2\mathrm{H_2O} \longrightarrow & 6\mathrm{Fe^{2+}} + & \mathrm{SO_4^{2-}} + & 10\ \mathrm{OH^-} \\ 4.62 & 0.77 & 1.54 & 4.62 & 0.77 & 7.70 \end{array}$$

Considering the large quantities of H^+ or OH^- formed, the assumption of a local equilibrium is unlikely, as shown by reactions (1) to (4). By combining reactions (1) and (3), and (2) and (4) the following formulas are derived in which the production of hydrogen and hydroxyl ions is negligible:

$$\begin{array}{lllllllllll}
(5) & 24\ \mathrm{FeOOH} & + & \mathrm{FeS} & \rightarrow & 8\mathrm{Fe_3O_4} & + & \mathrm{Fe^{2+}} & + & 12\ \mathrm{H_2O} & + \ \mathrm{SO_4^{2-}} \\
 & 18.48 & & 0.77 & & 6.16 & & 0.77 & & 9.24 & \ \ 0.77
\end{array}$$

$$\begin{array}{lllllllllll}
(6) & 16\ \mathrm{FeOOH} & + & \mathrm{S} & \rightarrow & 5\ \mathrm{Fe_3O_4} & + & \mathrm{Fe^{2+}} & + & \mathrm{SO_4^{2-}} & + \ 8\mathrm{H_2O} \\
 & 12.32 & & 0.77 & & 3.85 & & 0.77 & & 0.77 & \ \ 6.16
\end{array}$$

The observed proportions of SO_4^{2-}, Fe^{2+} and Fe_3O_4 among the late minerals do not agree with these results. According to Nagy (personal communications) some magnetite occurs in the veins but according to equation (5) or (6) magnetite should be a common vein mineral which is not the case. Further, processes like (1) to (6) require more iron than is present according to the bulk composition of the meteorite. It may be objected that sulphate-forming processes have been taking place in large volumes of the parent body and that the mobile sulphate has been enriched in certain parts of the parent body, but this can probably only account for some vein sulphate and not for the main part of the sulphate which is found in the groundmass.

Another explanation could be that the original groundmass had a chemical composition identical with the present gross composition of the meteorite. Aqueous solutions attacked the walls of fissures and reprecipitated dissolved fractions as sulphates without major redox processes. Such a leaching process might have taken place late in the development of the meteorite but it cannot explain how other late minerals or the original nonequilibrium assemblages of minerals in the groundmass were formed. The assumption of a closed system thus seems to be impossible.

Consequently the minerals were probably formed in an open system. The problem is to find an oxidizer strong enough to explain the formation of both sulphate and limonite.

It is possible that after primordial dust had formed a parental meteorite body reduction processes took place in the central part of the body (Ringwood, 1961) or in other hot zones (Anders, 1963; Fredriksson, 1963). Gaseous emanations like CO_2, CO and H_2O moved from these hot zones to the outer parts of the parent body. This may explain the origin of the water and CO_2. However, CO_2 is too weak an oxidizer to form goethite and sulphate from troilite, as can be observed in Figure 17 and equation 7.

$$(7) \quad H_2O_{(\ell)} + CO_{2(g)} + FeS \rightarrow FeOOH + CO_{(g)} + 1/2\ H_{2(g)} + S_{(s)}$$

$$\underset{\sim}{\Delta G_r} = +22.41\ \text{Kcal}$$

Nor is it likely that thermal decomposition of water into oxygen and hydrogen can explain the redox processes, since the presence of goethite and gypsum show that the reactions took place at very low temperatures where the dissociation of water can be considered negligible, (Wagman, et al, 1945, see Table 4c). Nor is it likely that any of the reactions (8) to (12) played any important role:

Reaction	Free energy of reaction ΔG_r (Kcal)
(8) $S + H_2O_\ell \rightarrow H_2S_{(g)} + 1/2\ O_2$	+47.5
(9) $S + 4H_2O_\ell \rightarrow H_2SO_{4aq} + 3H_{2(g)}$	+49.42
(10) $2H_2O_{(\ell)} + Fe_3O_4 \rightarrow 3FeOOH + 1/2\ H_{2(g)}$	+0.68
(11) $FeS + 2H_2O_{(\ell)} \rightarrow FeOOH + S_{(s)} + 1\ 1/2\ H_{2(g)}$	+15.60
(12) $FeS + 2H_2O_{(\ell)} \rightarrow FeOOH + H_2S_{(g)} + 1/2\ H_{2(g)}$	+7.71

Certainly equation (10) can explain how limonite was formed from magnetite but it does not explain the formation of native sulphur or sulphates or the corroded nature of the troilite. Equations (11) and (12) can to some extent explain this, but the free energies of reaction seem to be fairly large, particularly for (11) which is the only one that might explain the formation of both limonite and sulphur from troilite. Nor has this reaction been observed in any hydrothermal experiments; instead FeS seems to alter to hydrotroilite (Moh and Kullerud, 1964). However, since the system is open, the hydrogen formed may escape from the system and thus make reactions like (11) more likely, but this would also mean that water can escape.

Another explanation would be that oxides present in primordial dust acted as oxidizers, but as was pointed out by Latimer (1950) the primordial dust must in the main have been characterized by rather reducing conditions since the quantities of oxygen present were small. Another strong argument against such an explanation is that the Orgueil meteorite as we see it today is the result of long and complex processes. It therefore seems unlikely that the oxidation state of the primordial dust could have any influence on late mineral-forming processes in the meteorite parent body.

Consequently it seems questionable if emanations from the inner part of the meteorite parent body or the composition of the primordial dust can explain the redox processes in the Orgueil meteorite.

A third possible explanation would be that water on the surface of the meteorite parent body has been exposed to ultraviolet radiation from the sun. This dissociates some of the water into several chemical compounds and radicals. The fast-diffusing hydrogen may escape from the surface at a more rapid rate than the heavier radicals and compounds of oxygen, part of which dissolve in the surface water and oxidize the upper layers of the meteorite parent body. This process was suggested by Poole (1941) as a geochemically important process for the earth. These reactions have been more extensively discussed by Harteck and Jensen (1948) and Dole (1949). It seems likely that these processes could occur on a meteorite parent body. Some support for such an assumption is found in the tuffaceous structure of the meteorite, and the hydrated nature of the minerals, indicating that they have been formed close to the surface. Further the mixture of redox states in the Orgueil meteorite resembles the surface conditions on the earth. In terrestrial unconsolidated rocks and soils, oxidized and reduced phases like limonite and bitumen are often mixed together. This depends on the fact that at low temperatures and pressures many systems approach equilibrium very slowly. The process can explain the observed quantities of sulphate, magnetite and limonite, but requires that the gravitational field was sufficiently large to retain the gaseous oxidizing emanations and liquid water, at least for some time. A geologically short period of oxidizing conditions should suffice to explain the processes discussed above, perhaps some 1000 years as is indicated by the crystallization time for dolomite as suggested by DuFresne and Anders (1962, p. 1085). For such a short time even fairly small celestial bodies should be able to retain an atmosphere according to the calculations by Spitzer (1952) and Sytinskaya (1962) but it seems questionable if this celestial body can have been much smaller than the moon.

It could be proposed that oxygen was formed by living organisms as a product of carbon dioxide assimilation. However, the evolution of life and the subsequent formation of oxygen as a result of biological activity is a process that demands much longer time than the interaction between water and ultraviolet radiation, or some other kind of energetic radiation that can dissociate water. This also means that the parent body must be able to retain the atmosphere longer, perhaps some 100,000 years and consequently must be of larger size under otherwise identical conditions.

Oxidation processes involving free oxygen may lead to acid conditions. This is evident from the reactions (13) to (15). Organic matter could react with oxygen, forming water and carbon dioxide. The resulting acids could react with several phases, like brucite, forming late sulphates and carbonates according to reactions (16) and (17):

	Reaction	Free energy of reaction ΔG_r (Kcal)
(13)	$2H_2O + 2S + 3\ O_2 \rightarrow 2H_2SO_4$	-241.3
(14)	$2H_2O + 2FeS + 9/2\ O_2 \rightarrow Fe_2O_3 + 2H_2SO_4$	-371.8
(15)	$3H_2O + 3FeS + 13/2\ O_2 \rightarrow Fe_3O_4 + 3H_2SO_4$	-534.4
(16)	$H_2SO_4 + Mg(OH)_2 + 7H_2O \rightarrow MgSO_4 \cdot 7H_2O + 2H_2O$	<-17.3
(17)	$H_2CO_3 + Mg(OH)_2 \rightarrow MgCO_3 + 2H_2O$	-11.1

Certainly many processes like (13) to (17) can be considered. There is as yet little evidence of these reactions and therefore the qualitative discussion given above must suffice.

It should be remembered that these conditions do not imply that an oxygen-rich atmosphere or a strongly acid surface layer was formed; it seems more probable that the oxygen and the acids were consumed immediately after their formation.

It is also probable that redox processes were acting when the chlorite in its present state was formed, since chemical analysis, Table 1, as well as diffraction data suggest a high content of ferric iron (see p.3-5). The parent material of the chlorite is not known but might have been a well-ordered ferrous chlorite, formed together with troilite and magnetite under hydrothermal conditions. Later oxidizing processes formed solutions rich in ferric iron and sulphate which could react with the early chlorite and transform it to the present chlorite. The sulphate and ferric ions may be delivered from the oxidation of troilite, which at the same time also could form native sulphur and limonite. Some oxygen may also have reacted directly with ferrous chlorite forming ferric chlorite. Limonite has not been observed in the veins; it is therefore probable that the oxidizing processes were declining in intensity or had ceased completely when the veins were formed. However, another explanation for the absence of limonite in the veins may be that since the solubility product for ferric hydroxide is very small the ferric iron could not migrate long distances before it was precipitated. It may also be suggested that limonite was formed from lawrencite, $FeCl_2$, after the fall of the meteorite. It is difficult to visualize, however, how lawrencite could survive the redox processes that formed ferric chlorite.

It has been suggested that alteration of olivines and pyroxenes of chondritic composition could form chlorite and brucite, (Kerridge, 1964) but the high content of volatile elements like mercury, lead and bismuth (Anders, 1964) makes it unlikely that the present groundmass has been exposed to magmatic temperatures. Another suggestion would be that periclase and olivine were mixed with the low-temperature phases, a process similar to the one that formed Murray (Fredriksson and Keil, 1964) and that periclase later was hydrated to brucite.

6. Conclusions

From the above discussions it is apparent that the Orgueil meteorite does not represent original solar material. On the contrary the meteorite has undergone extensive hydrothermal and low-temperature alterations, although these processes seem not to have changed the bulk chemical composition of the primitive, that is the pre-Orgueil, material seriously. The reason for this conclusion is that it has still a bulk composition which resembles the assumed solar composition (Suess and Urey, 1956; Aller, 1961; Anders, 1964). As has been discussed above, a high temperature magmatic pre-Orgueil stage can be practically ruled out, at least for the major fraction.

The following sequence of events for the development of the Orgueil may be suggested. A presumed primitive accumulation of dust, frozen gases, ice, etc. (Urey, 1952, 1963; Ringwood, 1960; Anders and DuFresne, 1962; and others) probably of the size of a large asteroid or possibly as big as the moon developes hot zones either by short lived radioactivity or possibly by slow collisions, that is, between bodies of which at least one has a very low density. One of the colliding objects might even have been a comet head as advocated by Urey (1963), and Urey and Murthy (1963). Conceivably, in such a collision, the energy may be dissipated relatively slowly within the larger body. Once formed it seems possible that such hot zones could be enforced by chemical reactions, possibly between free radicals* (Urey, 1952). If the dust planetoid was penetrated deep enough by the shockwaves, large

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*Recently free radicals were found in the Mighei, group II, carbonaceous chondrite (Vinogradov, et al, 1964).

quantities of magma may have been generated and retained for a sufficient time to give rise to processes resembling volcanism. As suggested by Ringwood, 1961; Fredriksson, 1963; and Fredriksson and Ringwood, 1963, chondrules may well be the product of such explosive volcanism. Some chondrule may also form directly as splash drops (Urey and Craig, 1953, a.o.). The heat from the hot zone would influence the surrounding primitive material (Anders, 1963); hot gases will be driven towards the surface creating pneumatolytic to hydrothermal conditions such that troilite (FeS) might crystallize, together with other minerals, probably layer lattice silicates. The latter minerals probably were the parent material for the present Orgueil matrix silicate, the chlorite. During the cooling-off period the troilite oxidizes to limonite, sulphur, and sulphate. At the same time the late carbonates and sulphates formed and the chlorite acquired its present composition. As has been shown it is probably necessary to assume an external source of oxidation, possibly free oxygen. This oxygen would be supplied by dissociation of water induced by ultraviolet light at the surface of the body. The surface is continuously reworked by the impact of smaller bodies or secondary objects produced in larger collisions. Such processes are vividly suggested by the Ranger pictures of the moon. The reworking of the surface would expose a considerable amount of Orgueil material to sunlight. Close to the volcanic area (or areas) where pre-Orgueil material may be mixed with chondrules and heated to higher temperatures similar processes may further account for meteorites like Murray (Fredriksson and Keil, 1964) which is a mixture of chondrules and mineral fragments of high temperature origin (Fredriksson and Reid, 1965) and low temperature phases similar to the bulk of the Orgueil.

APPENDIX

1. Notation

(A)	Activity of A
F	Faraday constant
G_r	Free energy of a reaction
H_f	Heat of formation
K	Thermodynamic equilibrium constant
P	Pressure
R	Gas constant
S	Entropy
T	Absolute temperature
e^o	Standard electrode potential
n	Number of Faradays
pA	Negative decadic logarithm of (A); thus $pH = -\log_{10} (H)$ $pFe_{tot} = -\log_{10} (Fe_{tot})$
pK	Negative decadic logarithm of K
In	$\log_e$

APPENDIX

2. Calculation of the physico-chemical constants

The standard redox potential and the equilibrium constant for a reaction are found by the expressions:

$$\underline{e}^{o} = \frac{\Delta G_r}{\underline{n}\ \underline{F}}$$

and

$$\ln \underline{K} = \frac{\Delta G_r}{-\underline{R}\ \underline{T}}$$

Almost all values for ΔG, ΔH and S for 25°C, 1 atm. are derived from Latimer (1952) with exception for the values $\Delta H_f = 813.13$ K cal, S = 87.7e.u. for $MgSO_4 \cdot 7H_2O$ that were calculated by means of data in Kelley (1937, p. 101), and Latimer (1952, p. 316, 359-369), and the value $\Delta G_f = -117.0$ K cal for goethite (Schmalz, 1958).

Most of the calculations are for 25°C, 1 atm. conditions. A few 100°C calculations have been made by means of data from Kelley (1960) and by the formulas for the variation of ΔG with temperature given in Kortüm (1960, p. 398-410).

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FIGURE CAPTIONS

Fig. 1. Photomicrograph of thin section of Orgueil. Magnification X. Nicols half crossed to increase contrast. According to the probe analysis the fragment has a composition similar to the matrix except for somewhat higher nickel and sulphur. Note the parallel structures around the fragment, suggesting that the fragment was harder than the surrounding material during agglomeration.

Fig. 2. Electron micrograph of overlapping crystals of the layer lattice silicate (chlorite, see page 3) which constitutes approximately 3/4 of the meteorite. Note the pseudohexagonal habit of the crystals.

Fig. 3. Electron diffraction pattern of one of the crystals in Fig. 2. The deduced lattice spacings (in Å) $a = 5.28, b = 9.14$ agrees fairly closely with ferric chamosite, see page 5 , and Table 3.

Fig. 4. Photomicrograph of the magnetic fraction, 44-88μ, of a powdered sample of Orgueil. The shiny globules are native sulphur (S) closely associated with hexagonal troilite (FeS). Note particularly the corroded troilite crystals, two of which have holes. Two opaque black spherules as well as some of the aggregates consist of magnetite (Fe_3O_4).

Fig. 5. a,b. X-ray micro-radiographs of a thin section of Orgueil, a) in CuKα radiation and b) in CrKα radiation. The particles indicated with A consist of magnetite (Fe_3O_4) and those with B of troilite (FeS with some Ni). The absorption in magnetite as compared with the matrix is considerably decreased for CrKα while troilite, B,

shows same or increased contrast in this radiation. Note the corroded hexagonal plate of troilite, lower right.

Fig. 6. *a*,*b*. Micro-radiographs (compare Fig. 5) showing rounded hollow particles of magnetite (Fe_3O_4). The small hexagonal particle upper left is troilite.

Fig. 7. Photomicrograph and electron probe scanning pictures of corroded troilite, partly altered to ferric hydroxides, limonite. The back scattered electron picture (BSE) indicates the average atomic number of the phases present, the three other scan pictures show distribution of iron, sulphur and nickel. Most of the opaque grains are magnetite. Note that nickel is homogeneously distributed in the matrix; the concentration is approximately 1%, almost the same as in troilite and limonite (p. 8-9). Sulphur is also present in the matrix but less evenly distributed than nickel; the sulphur probably occurs as a sulphate impregnation of the layer lattice silicate. The scanned area, $\sim$50 x 50 microns, is indicated on the photomicrograph.

Fig. 8. *a*, *b*. Photomicrograph of thin section of powdered sample of Orgueil; magnetic fraction 44-88 microns. A is transmitted light; B reflected light. The pictures illustrate the close association of native sulphur, transparent in A, whitish gray in B, with troilite. B further illustrates the extremely corroded state of the hexagonal troilite crystals which explains their odd shapes and colors.

Fig. 9. Electron probe scanning pictures of polished section of Orgueil, showing one grain $\sim$10 microns, of periclase MgO, possibly formed by vacuum and heating in the electron microprobe, see page 13. All the

iron-rich grains, white in the back scattered electron (BSE) as well as in the iron picture, are magnetite, as concluded from the deficiency in sulphur. Sulphur is rather homogeneously distributed through the matrix. The magnesium-rich grain to the left gave an analysis corresponding to a mixture of magnesium hydroxide and magnesium sulphate. Scanned area approximately 100 x 100 microns.

Fig. 10. Distribution of Na^{23}, Mg^{24}, Mg^{25}, and Si^{28}, in polished sections of Orgueil. The pictures were obtained by means of secondary ion emission spectroscopy (Castaing and Slodzian, 1962a and b, and 1963). The pictures illustrate composite veins of magnesium and sodium sulphates. The veins are enriched in sodium, particularly at the vein walls. The matrix material also contains small amounts of evenly distributed sodium. Note that no direct comparison between different elements can be made on the basis of the recorded intensities. The black grid represents strips of aluminum evaporated onto the sample to overcome its low conductivity. The size of the square holes is approximately 50 x 50 microns.

Fig. 11. Photomicrograph of thin section of Orgueil showing several hexagonal limonite particles representing completely altered troilite crystals. Compare Figures 5 and 7 and page 15 . These particles seem indistinguishable from organized elements, group V (Claus and Nagy, 1961).

Fig. 12. Phase relations in the system Fe-O-S between 560°C and 675°C. (After Kullerud, 1957).

Fig. 13. Phase relations in the system Fe-O-S below 560°C. (After Kullerud,1957).

Fig. 14. pH diagrams at 25°C, 1 atm. a) for the system H_2CO_3-H_2O, b) for the system H_2SO_4-H_2O.

Fig. 15. e-pH diagram for the system Fe-S-H_2O. There are no thermodynamic data available for hydrotroilite, FeS·nH_2O, which seems to be the stable form at 25°C and 100°C. The field for FeS in the diagram thus gives the minimum extension of the stability field for hydrotroilite. The stability field for goethite, FeOOH, is not indicated but is somewhat larger than that for Fe_2O_3. Small figures attached to the lines indicate to what pS_{tot} value the lines refer; pFe_{tot} = 2. a) for 25°C, 1 atm; b) for 100°C, 1 atm.

Fig. 16. e-pH diagram for the system Fe-H_2CO_3-H_2O. Small figures attached to the lines indicate to what $pH_2CO_{3\ tot}$ value the lines refer; pFe_{tot} = 2. Shaded areas indicate where carbonates and sulphates may be stable together. a) for 25°C, 1 atm; b) for 100°C, 1 atm. The stability field for goethite, FeOOH, is not indicated but is somewhat larger than that for Fe_2O_3.

Fig. 17. e-pH diagram for the system S-H_2O at 25°C, 1 atm. Small figures attached to the lines indicate to what pS_{tot} value the lines refer.

Fig. 18. e-pH diagram with the systems Fe-H_2O and H_2O-C superimposed on each other at 25°C, 1 atm. pFe_{tot} = 2. The stability field for FeOOH, is not indicated but is somewhat larger than that for Fe_2O_3.

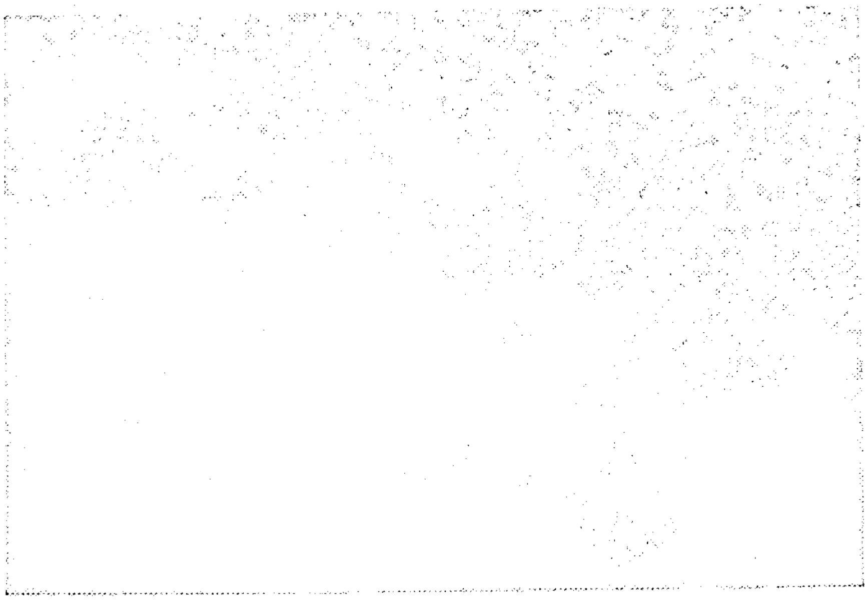


Fig.-1a

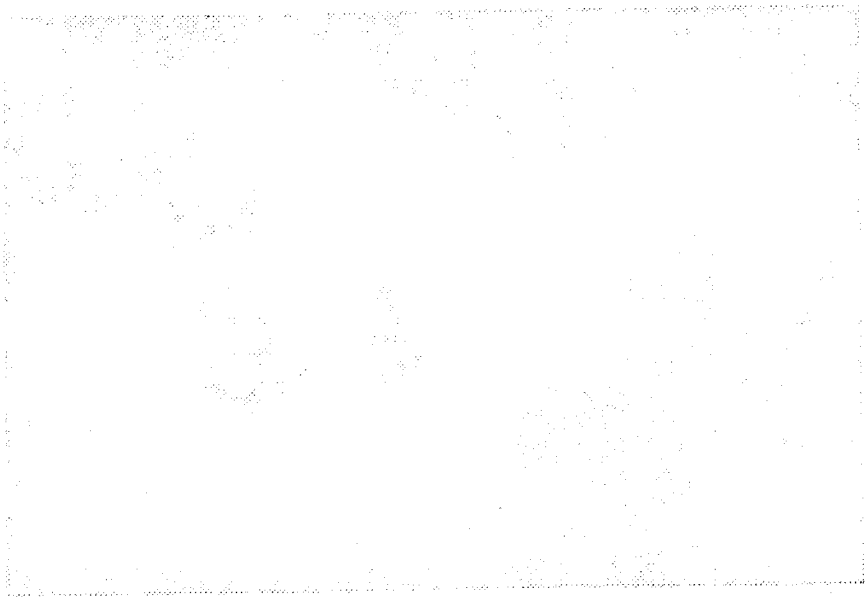


Fig.-1b

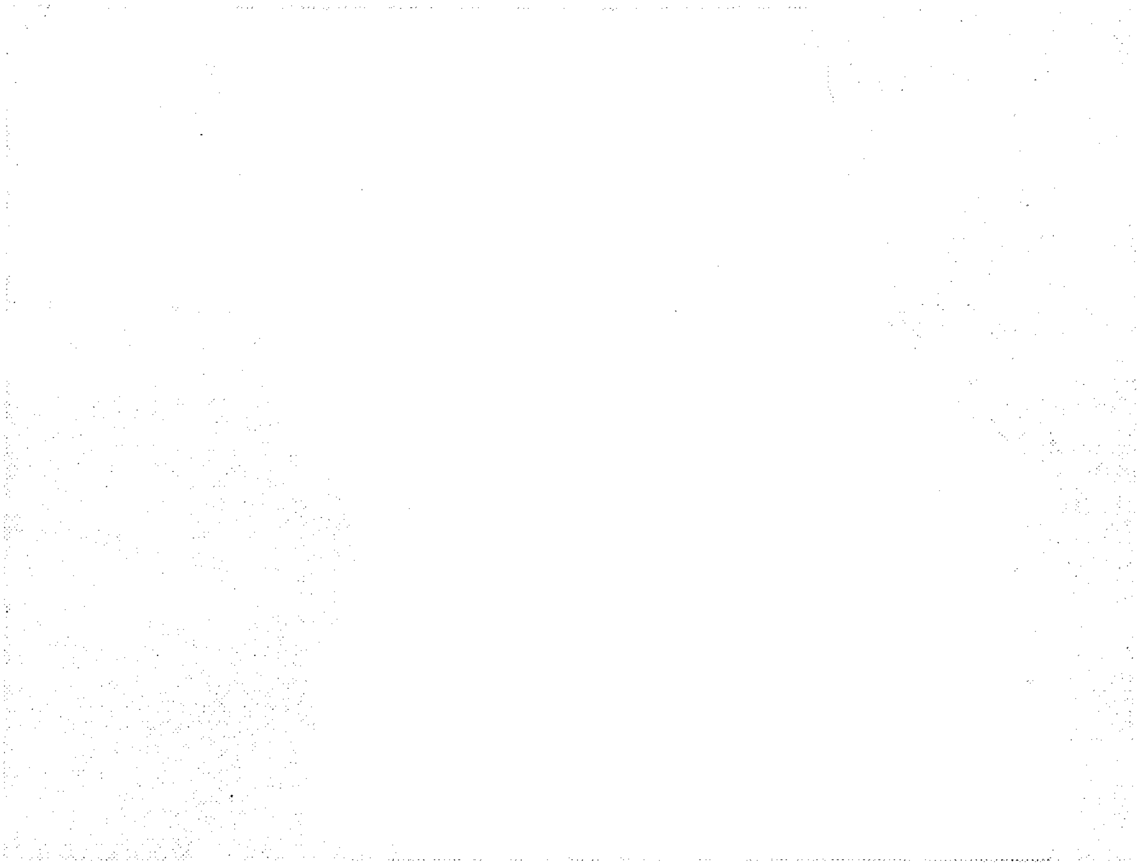


Fig.-2

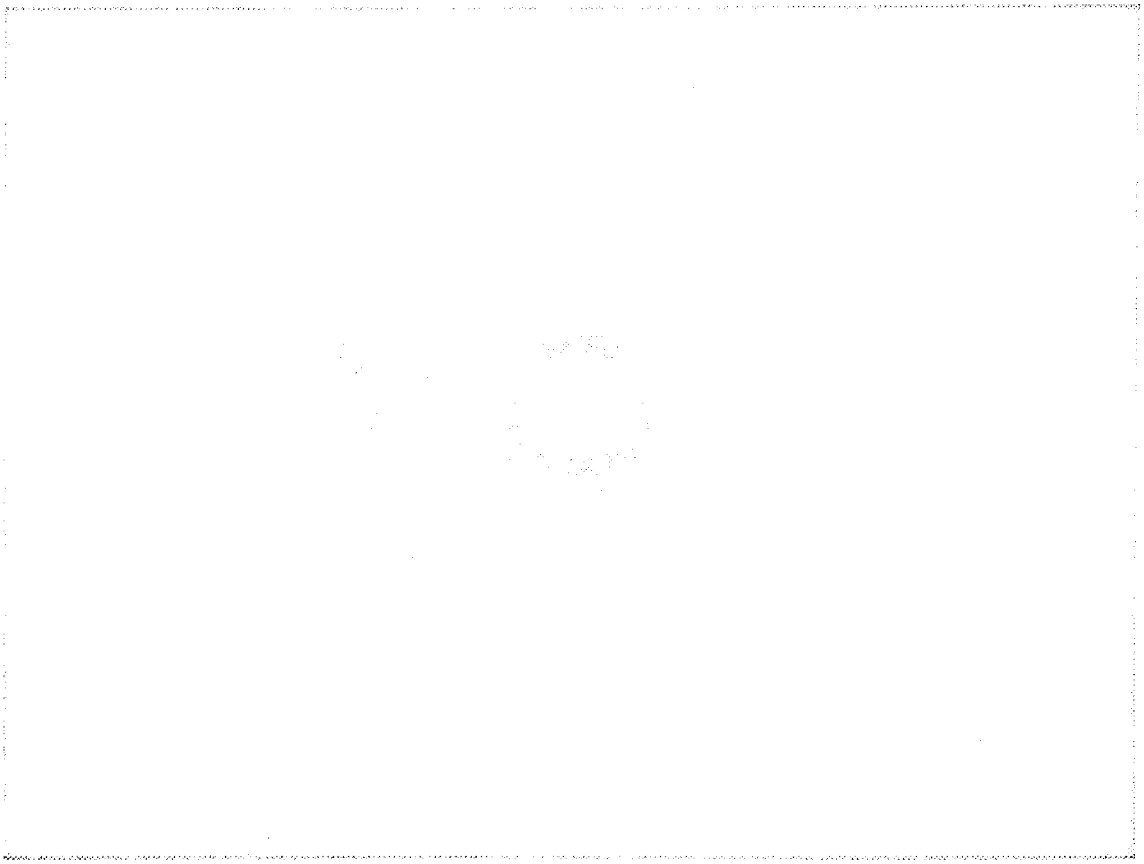


Fig.-3

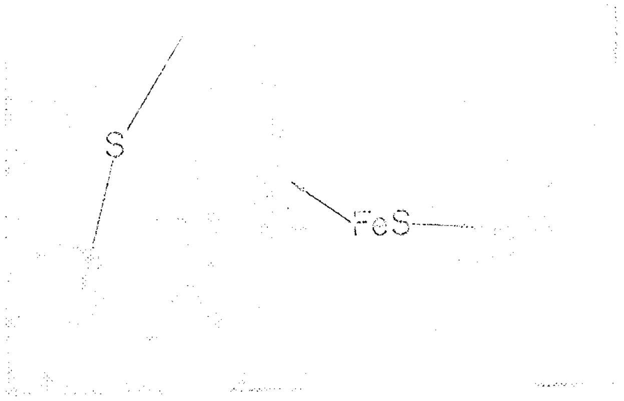


Fig. 4

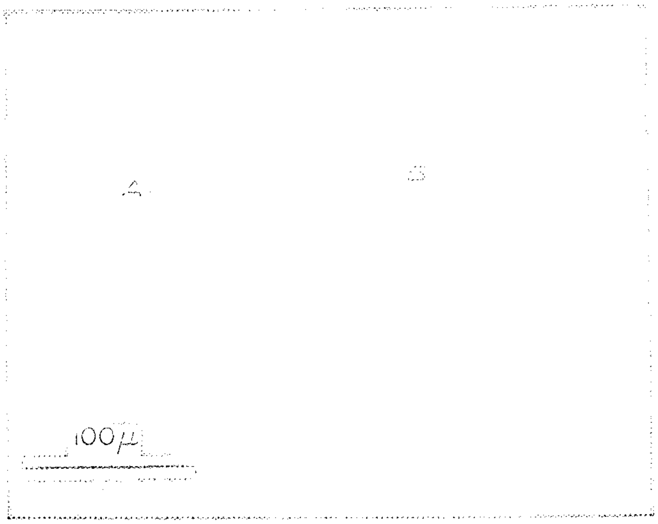


Fig.-5A

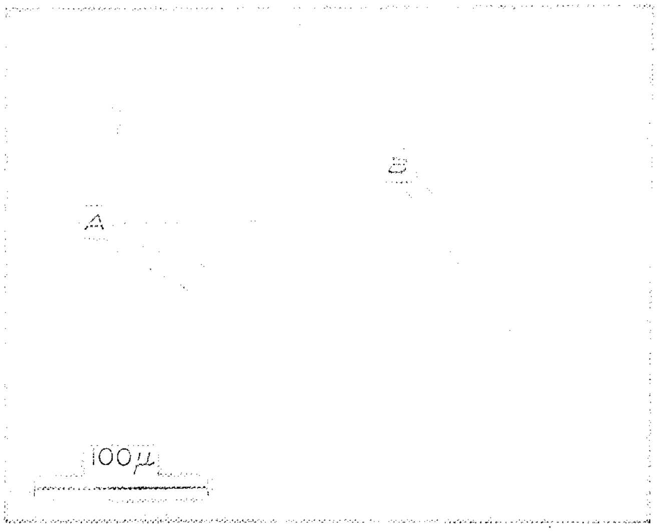


Fig.-5B

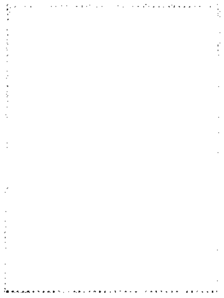


Fig.-6A

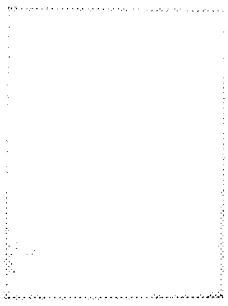


Fig.-6B

Fig.-7

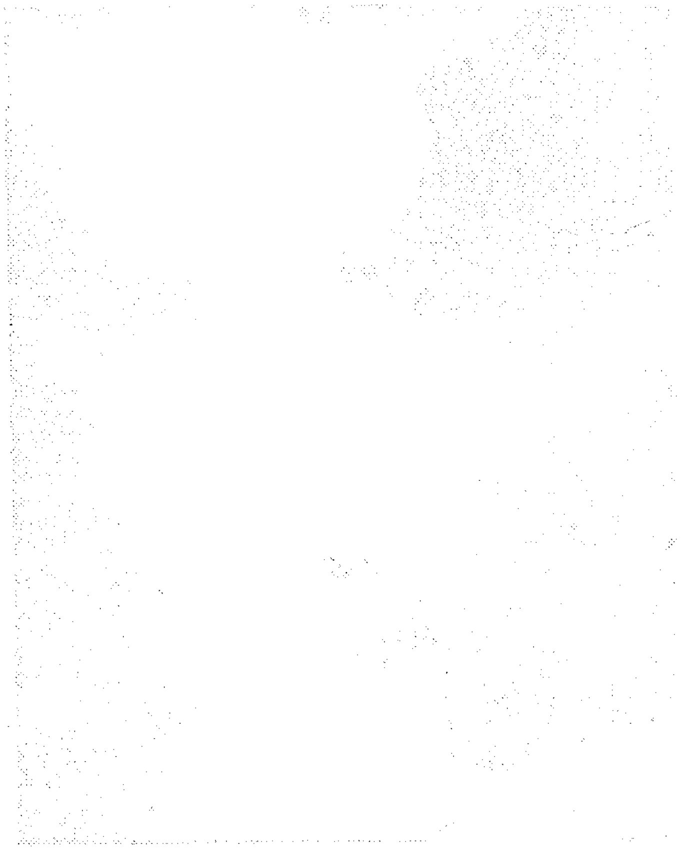


Fig.-8a

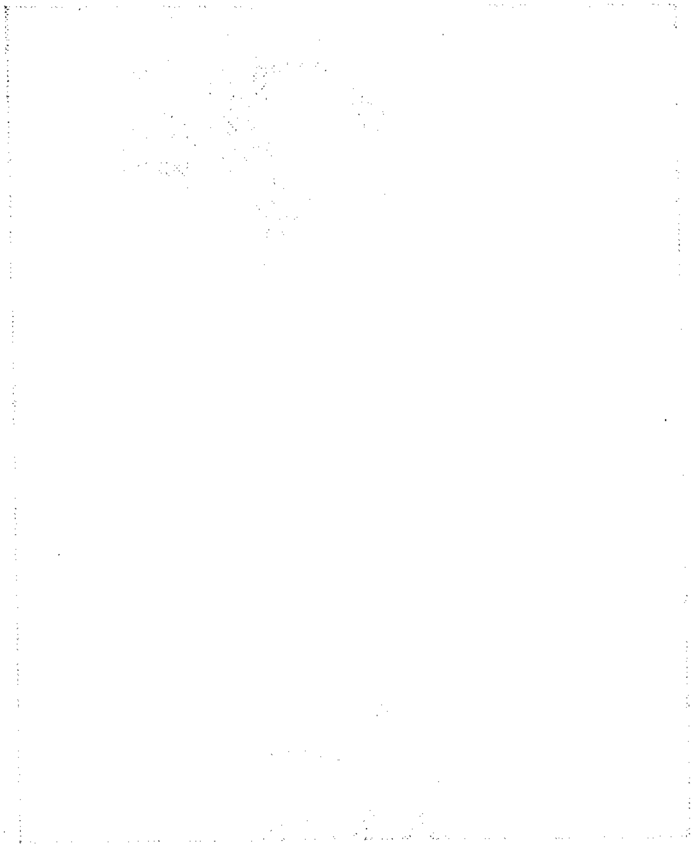
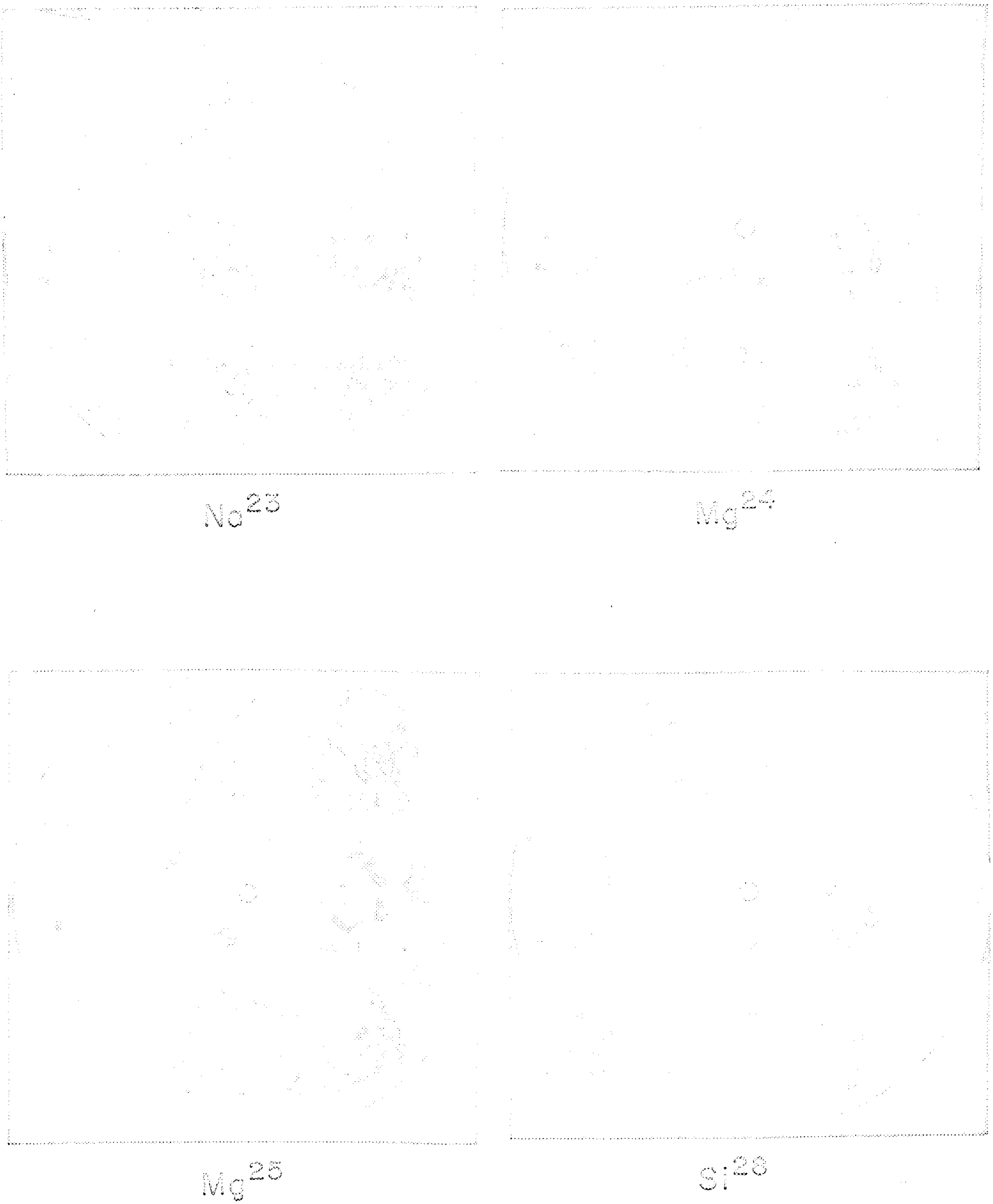


Fig.-8b



Na^{23} Mg^{24}

Mg^{25} Si^{28}

Fig.-9

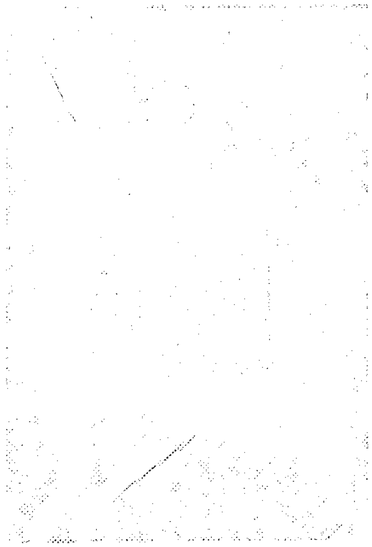
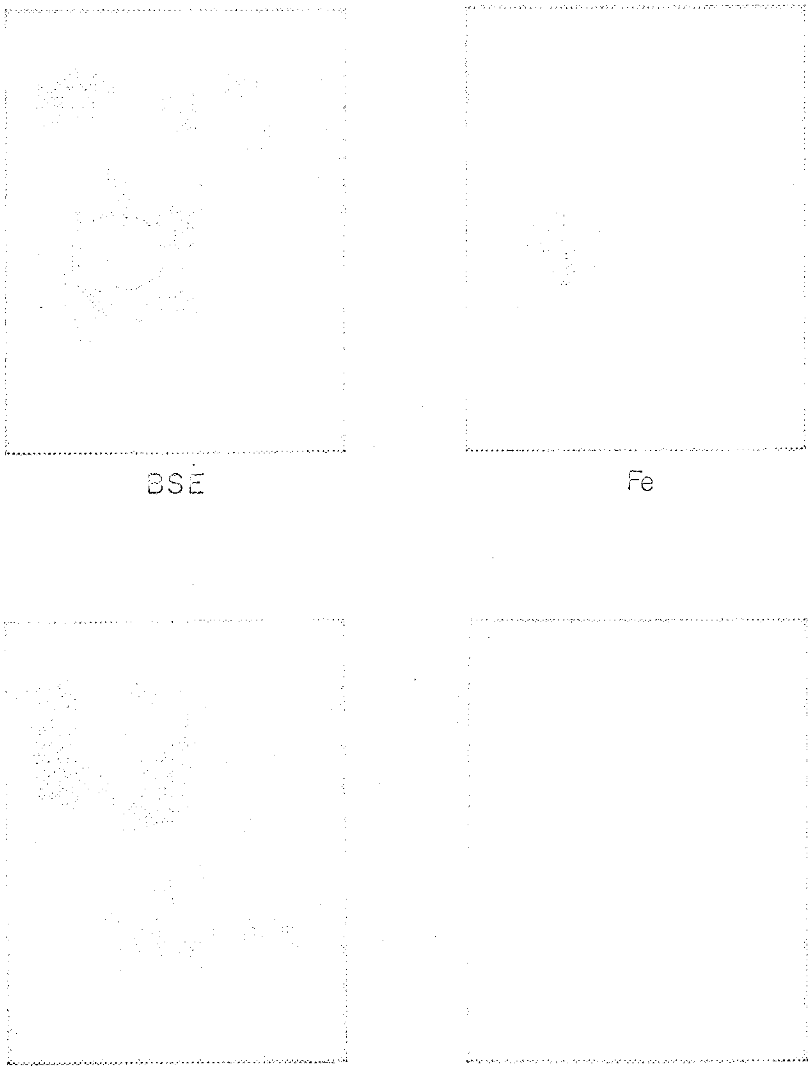


Fig.-11



BSE

Fe

S

Mg

Fig.-10

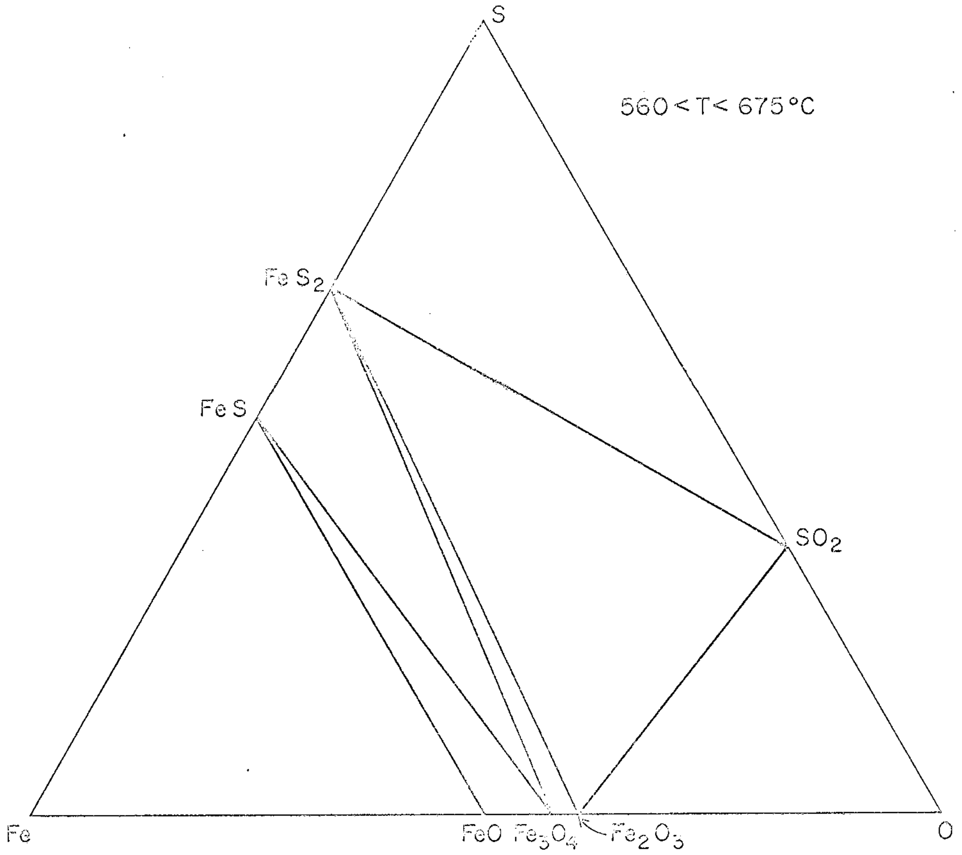

S
560 < T < 675 °C
Fe S2
Fe S
SO2
Fe
FeO
Fe3O4
Fe2 O3
O

Fig.-12

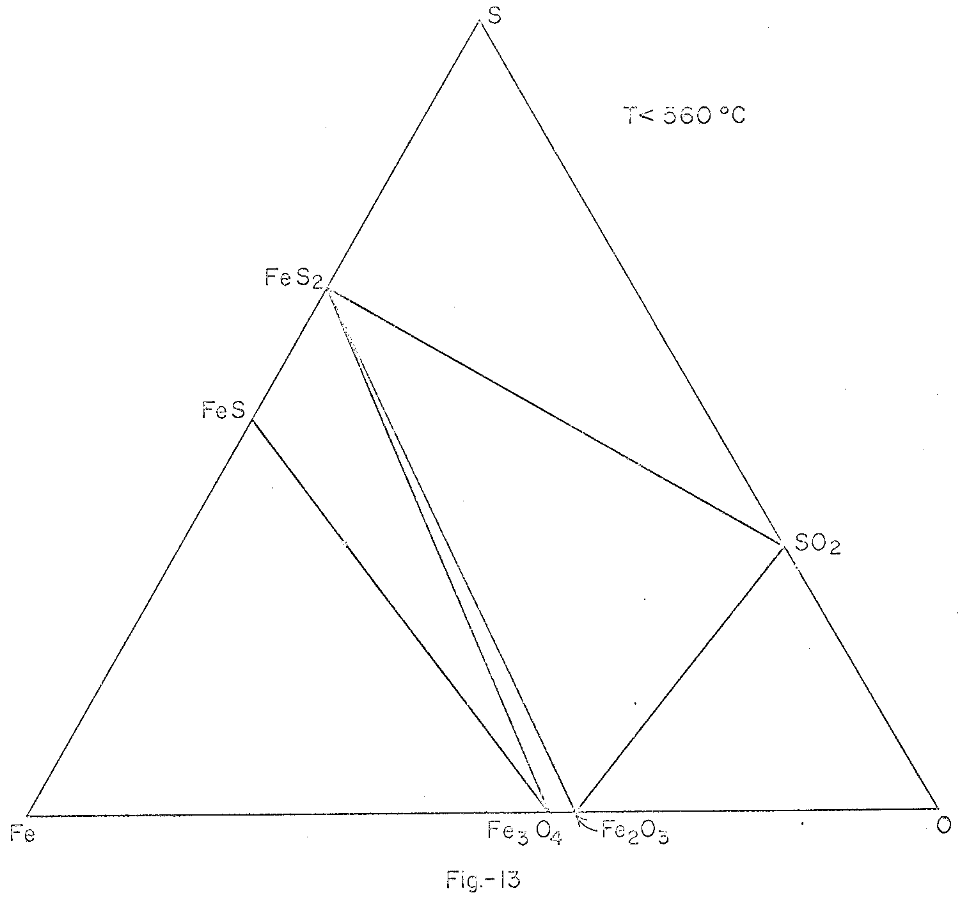

S
T< 560 °C
Fe S2
Fe S
SO2
Fe
Fe3 O4
Fe2O3
O

Fig.-13

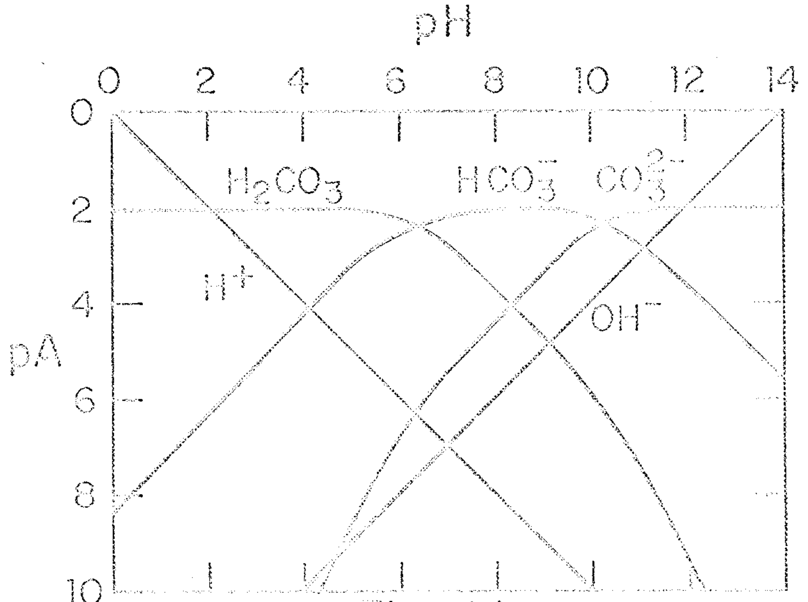


Fig.-14a

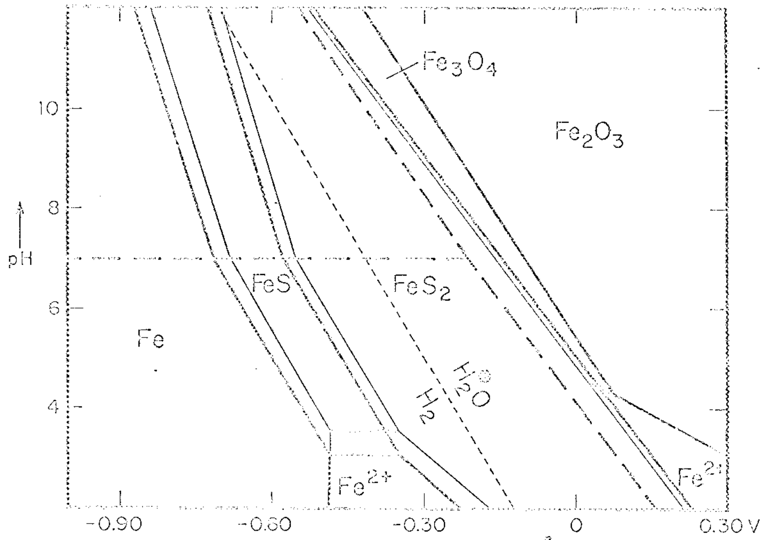


Fig.-15a

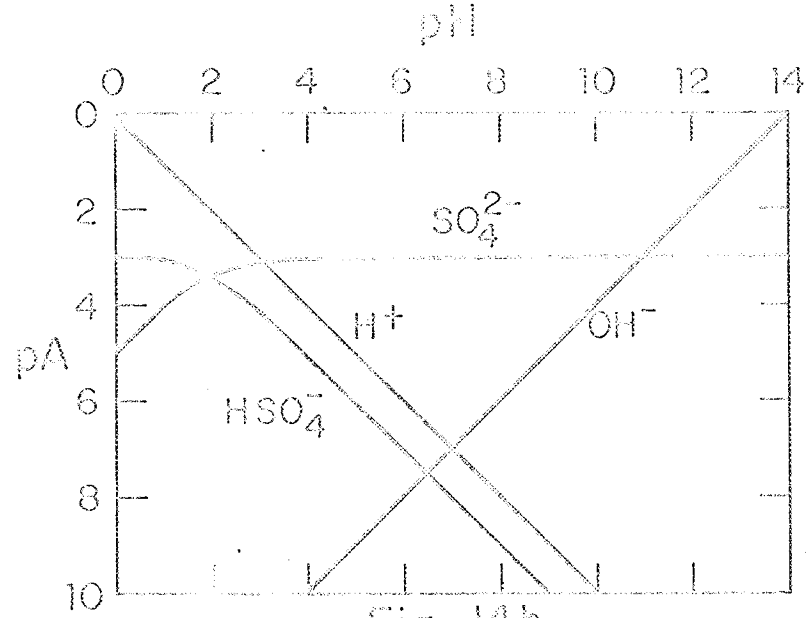


Fig.-14b

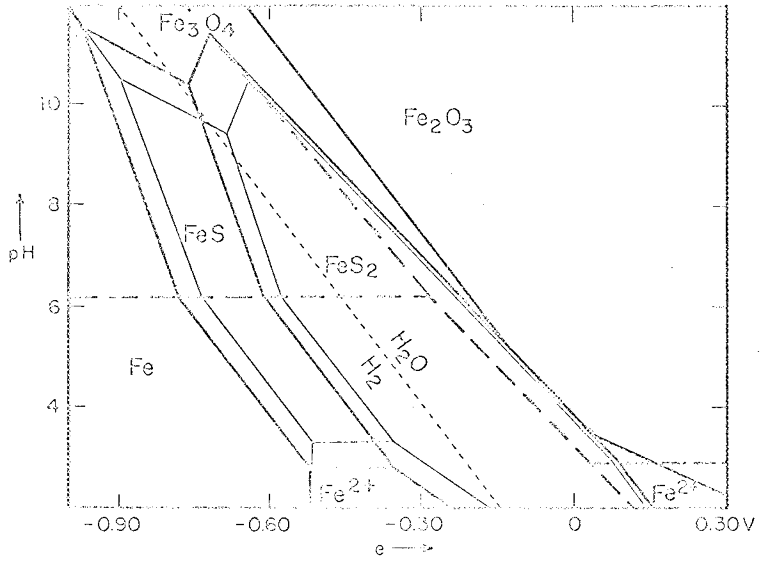


Fig.-15b

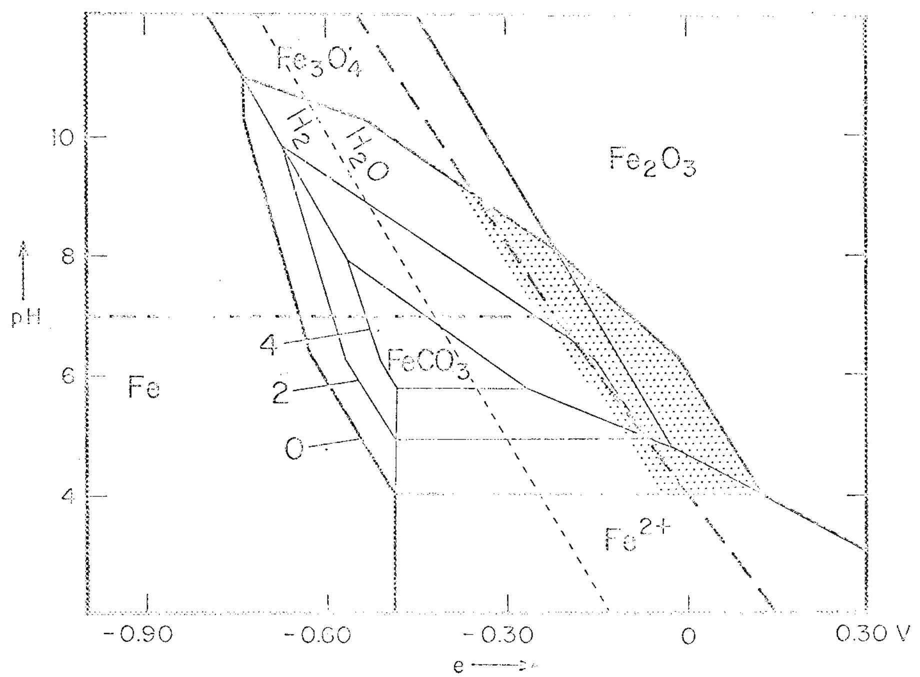


Fig.-16a

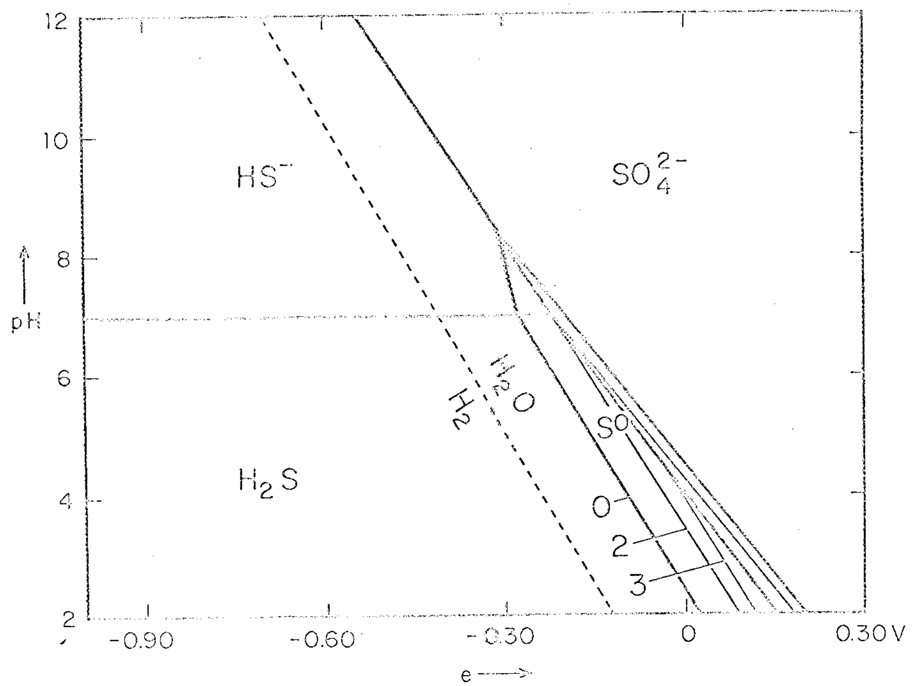
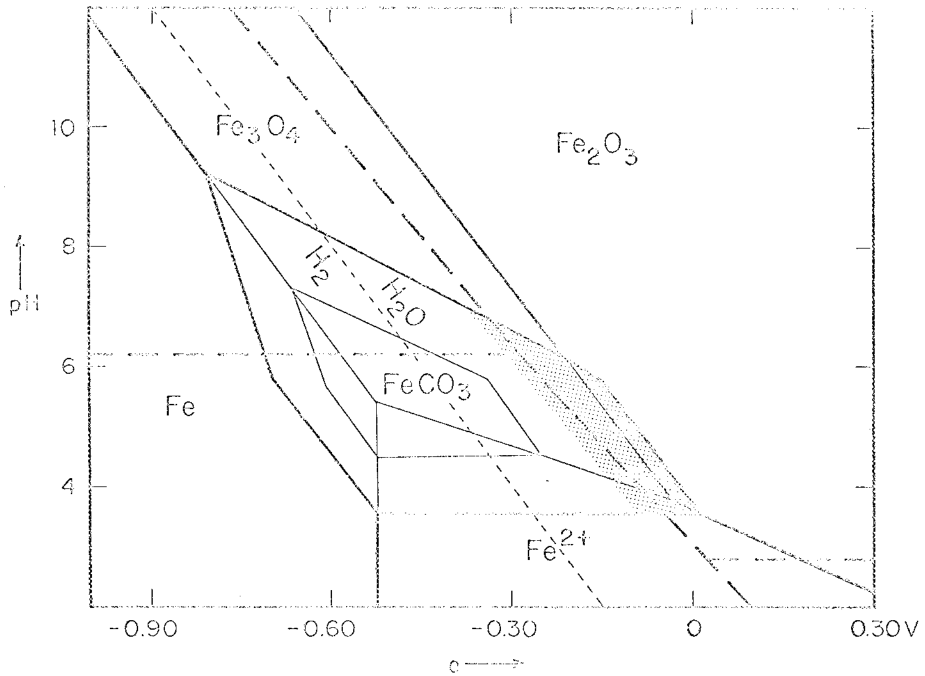


Fig.-17



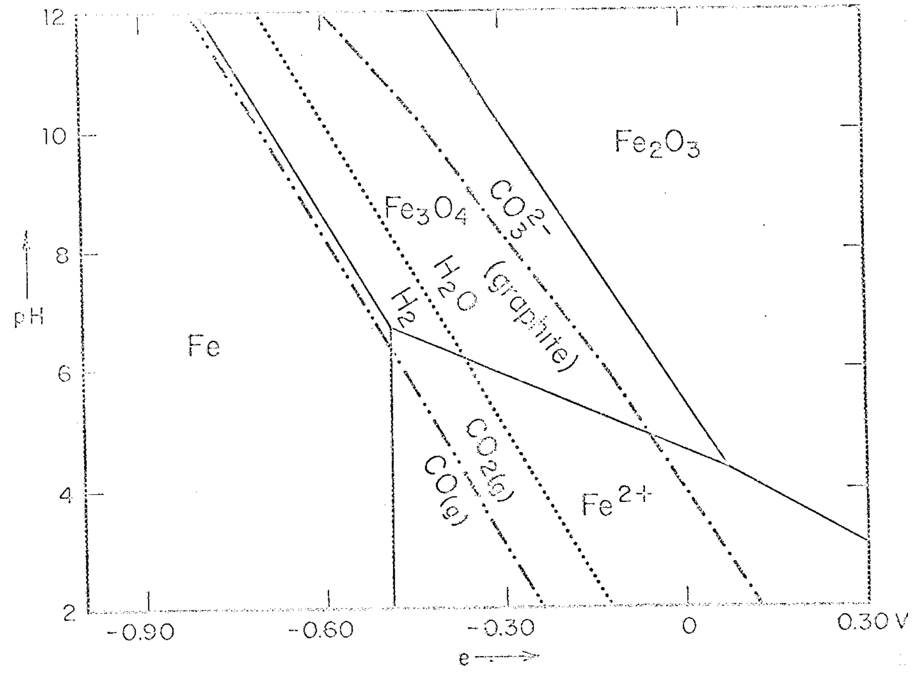


TABLE 1

Analysis in weight percent of chlorite

Si	14.9
Fe	15.6
Mg	12.9
Ni	1.4
Al	1.0
S	2.7

TABLE 2

Partial analysis of the Orgueil meteorite*

	% of total sample
Carbon-tetrachloride and ether extracts	3.2%
Sulphur in this extract	1.6%

Water-soluble matter	18.2%
Sulphate from this extract	6.9%
Magnesium from this extract	1.3%

Fe^{2+}	5.59%
Total Fe	18.31%
Fe^{3+} (by difference)	12.72%

---

*Analysis by E. Jarosewich, 1965, Division of Meteorites, Smithsonian Institution, Washington.

TABLE 3

Cell Dimensions (in Å)

	a	b	c	d_{001}
Found in Orgueil	5.28±0.05	9.14±0.09		7-14*
Serpentines**				
Chrysotile (ortho-)	5.34	9.2	14.63	
Lizardite	5.31	9.20	7.31	
Septechlorites**				
Amesite	5.31	9.19	14.01	
Ferrous Chamosite	5.415	9.38	7.11	
Ferric Chamosite	5.255	9.10	7.062	
Chlorites***				

$$a = 5.320 + 0.008\,(Fe^{2+} + Fe^{3+})$$

$$b = 9.202 + 0.014\,(Fe^{2+} + Fe^{3+})$$

$$d_{001} = 13.925 + 0.115\,(Si-4) - 0.025\,Fe^{3+}$$

---

* The d_{001} value from Nagy, et al, (1963), p. 544.

** From Deer, Howie, and Zussman (1962), p. 167, 174.

***Simplified from Hey (1954).

TABLE 4

Composition of the Orgueil meteorite

4a

	moles per 1000g (ignition loss free matter)
Fe	3.522
S	1.830
Si	4.009
Ti	0.009
Al	0.346
Mn	0.029
Mg	4.185
Ca	0.232
Na	0.255
K	0.016
P	0.042
H_2O	11.784
Cr	0.051
Ni	0.176
Co	0.009
C	2.755

4b

	moles per 1000g (ignition loss free matter)
native sulphur	0.542
sulphate, SO_4^{2-}	0.771
water-soluble magnesium, Mg^{2+}	0.559

4b (Cont'd)

ferric iron, Fe^{3+}	2.444
ferrous iron, Fe^{2+}	1.074

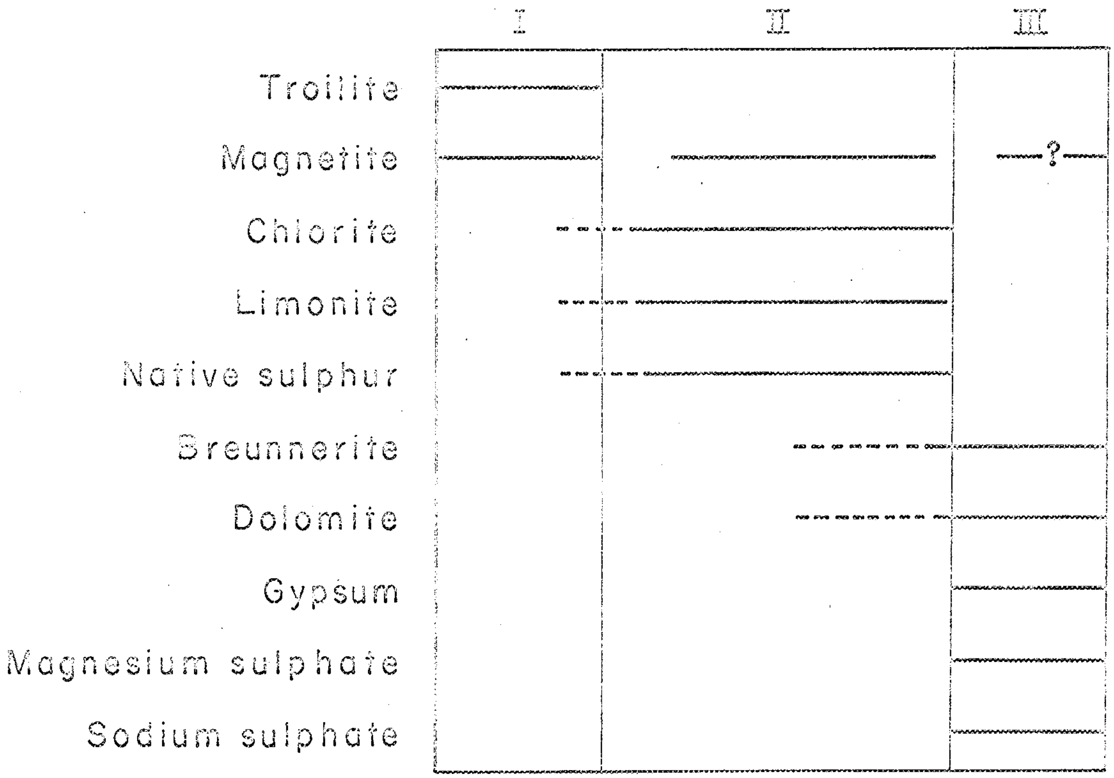
4c

Calculated quantities of the minerals in Orgueil

	Weight %
chlorite	62.6
magnetite	6.0
troilite	4.6
sulphur	1.7
limonite	0.5
merrillite	0.8
breunnerite	2.8
magnesium sulphate - x H_2O	6.7
gypsum	2.9
sodium sulphate	0.6
graphite	2.9
remaining metals	1.1
	93.2

TABLE 5

The succession of the Orgueil minerals



The succession of the various minerals is indicated by full lines, dashed lines indicate possible extensions. I indicates early period with formation of high temperature minerals, the controlling temperature being several hundred degrees centigrade, II later stage with moderately high temperatures, probably not above 170°C, and water-rich environment. III represents late vein mineralizations formed in an aqueous environment at low temperature, probably below 40°C.

TABLE 6

Stability constants at 25°C, 1 atm.

6a. Aqueous equilibria

$(Mg^{2+}_{0.8}\ Fe^{2+}_{0.2})\ (CO_3^{2-}) = 3.2 \times 10^{-9}$ (breunnerite)*

$(Ca^{2+})\ (Mg^{2+})\ (CO_3^{2-})^2 = 4.5 \times 10^{-20}$

$(Ca^{2+})\ (CO_3^{2-}) = 4.7 \times 10^{-9}$ (calcite)

$(Ca^{2+})\ (SO_4^{2-})\ (H_2O)^2 = 2.4 \times 10^{-5}$

$(Na^+)^2\ (SO_4^{2-})\ (H_2O)^{10} = 8.7 \times 10^{-2}$

$(Mg^{2+})\ (SO_4^{2-})\ (H_2O)^7 = 4.2 \times 10^{-5}$

$(Mg^{2+})\ (OH^-)^2 = 8.9 \times 10^{-12}$

$(Fe^{2+})\ (SO_4^{2-})\ (H_2O)^7 = 1.3 \times 10^{-12}$

$(Ni^{2+})\ (SO_4^{2-})\ (H_2O)^7 = 3.5 \times 10^{-2}$

---

*Assuming $FeCO_3$ and $MgCO_3$ to form an ideal solid solution.

6b. Other equilibria

~~$Mg_3\ Si_4\ O_{10}\ (OH)_2$ (talc) $\rightarrow 3\ MgO + 4\ SiO_2 + H_2O_{(g)}$ $P_{H_2O} = 2.5 \times 10^{-68}$ atm.~~

~~$Mg(OH)_2 \rightarrow MgO + H_2O_{(g)}$ $P_{H_2O} = 5.8 \times 10^{-7}$ atm.~~

$4\ CO_2 + 3\ Fe \rightarrow Fe_3O_4 + 4\ CO$ $K = 3.1 \times 10^{-3}$

$HCO_3^- \rightarrow H^+ + CO_3^{2-}$ $K = 4.69 \times 10^{-11}$

6c. Dissociation constant of water at various temperatures[*]

Reaction	T°K	Equilibrium constant of formation, K_f
$H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(g)}$	300	6.1×10^{39}
	400	1.7×10^{29}
	500	7.7×10^{22}
	600	4.3×10^{18}

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[*] Data from Wagman, D. D., et al, (1945).

TABLE 7

Activities of ions at various pH values in an aqueous solution in equilibrium with the solid phases $Mg_{0.8}$ $Fe_{0.2}$ CO_3, Mg $SO_4 \cdot 7H_2O$ and Ca $SO_4 \cdot 2H_2O$.

	a	b	c	d
pH	10.1	7	5	4
(Fe^{2+})	1.2×10^{-3}	1.2×10^{-3}	3.8×10^{-3}	9.4×10^{-3}
(Mg^{2+})	4.8×10^{-3}	4.8×10^{-3}	1.5×10^{-2}	3.8×10^{-2}
(Ca^{2+})	2.7×10^{-3}	2.7×10^{-3}	8.7×10^{-3}	2.1×10^{-2}
(SO_4^{2-})	8.7×10^{-3}	8.7×10^{-3}	2.8×10^{-3}	1.1×10^{-3}
(CO_3^{2-})	5.3×10^{-7}	5.3×10^{-7}	1.7×10^{-7}	6.8×10^{-8}
(HCO_3^{-})	8.3×10^{-7}	1.1×10^{-3}	5.0×10^{-2}	1.3×10^{-1}
pH_2CO_{3tot}	5.9	2.9	1.3	0.9