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A STUDY OF THE INTERACTIONS OF IRON METAL, HAEMATITE AND CALCIUM CARBONATE BETWEEN 700 AND 1100°C IN A NITROGEN ATMOSPHERE USING MÖSSBAUER SPECTROSCOPY

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ABSTRACT

The present work reports the ^{57}Fe Mössbauer results of samples containing iron metal, haematite and calcium carbonate fired to 700, 900, and 1100°C in an atmosphere of nitrogen. The chemistry of the system is discussed in view of the nature of the species identified, and the results are compared to those previously reported for an iron containing ceramic glaze recipe fired under exactly the same conditions.

INTRODUCTION

The chemistry of a number of transition metal ions in stoneware type ceramic glazes has been investigated under different firing conditions using a variety of spectroscopic techniques [1]. The importance of the role played by calcium ions in determining the transition metal environment has been highlighted for a number of different systems. Of particular interest is a system containing equal stoichiometric amounts of iron metal and haematite fired with ceramic glaze raw materials (i.e. potash feldspar, whiting, and quartz) in an atmosphere of nitrogen. Samples fired to 1100°C are light grey powders whilst those fired to 1300°C are deep blue glazes. However, the Mössbauer spectra of these two samples are identical within experimental error, both giving a doublet with an isomer shift of 1.05 mm s^{-1} and a quadrupole splitting of 2.36 mm s^{-1}, indicating that there is only one iron(II) site present and that the chemical environment of this site is determined a long time before glass formation occurs. In view of this, it is of interest to see if this iron(II) site can be reproduced purely by the interaction of haematite with iron metal and whiting, one of the mineral forms of calcium carbonate. In the present work equal stoichiometric amounts of haematite, iron metal and whiting are fired to different temperatures, in an atmosphere of nitrogen, and the Mössbauer results of the quenched samples are reported.

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EXPERIMENTAL

Reagent grade iron metal and haematite were obtained from commercial sources. Whiting, the mineral form of calcium carbonate used in the present work, was obtained from Harisson and Mayer, Stoke on Trent. X-Ray analysis showed that it consisted exclusively of calcite with no aragonite component. Weighed samples of the dried materials were fired in porcelain crucibles in a Carbolite MFHT type furnace fitted with a gas inlet facility. Containment of a nitrogen atmosphere during a firing cycle was initially found to be difficult so a quartz beaker, fitted with a quartz gas inlet tube, was inverted over the porcelain crucible to form a small inner chamber. This enabled the samples to be maintained at the required temperature for a period of 2 h exclusively in an atmosphere of nitrogen after which they were cooled to room temperature by a steady stream of the cold gas. ^{57}Fe Mössbauer spectra were obtained at room temperature using a standard Mössbauer spectrometer working under constant acceleration conditions as previously described [2]. All isomer shifts are quoted with respect to iron metal. The spectra obtained in all cases were complex, all having a number of overlapping lines. As the line shape of a Mössbauer peak is known to be Lorentzian, the Fourier transform technique, as described by Stone [3], was initially used to resolve the spectra. This method is valid for obtaining the positions of the absorption peaks but is totally unreliable for estimating intensities. Therefore, the final interpretation of the spectra is based on a least squares fitting of Lorentzian lines using the values obtained from the Fourier transform computation as the initial estimates [4].

DISCUSSION

Mössbauer results

The chemistry of the system under investigation is clearly complex and no simple explanation for the Mössbauer results can be given. The best fit Mössbauer spectrum of a sample fired to 700° C (Fig. 1) indicates that this spectrum is made up of four sextets and a quadrupole doublet (Table 1). The isomer shifts of component A, +0.306 mm s^{-1}, and of component C, +0.332 mm s^{-1}, are in fairly good agreement with values previously reported for both α-Fe_2O_3 and γ-Fe_2O_3, i.e. +0.38 mm s^{-1} and +0.34 mm s^{-1}, respectively [5]. The magnetic hyperfine field of component A, 488 kG, is in excellent agreement with previously reported data for γ-Fe_2O_3 which quotes two hyperfine fields [6] of 488 kG and 499 kG which cannot be successfully resolved in the absence of an applied magnetic field. The presence of two iron sites, with a small difference in the magnitude of the internal fields experienced by the nuclei, would explain the rather large line width of this sextet, 0.509 mm s^{-1}, compared to three of the other components of this spectrum. Component A is therefore attributed to the presence of γ-Fe_2O_3 whilst component C, with an internal magnetic field of 507.2 kG and a quadrupole splitting of 0.119 mm s^{-1}, is attributed to the presence of α-Fe_2O_3

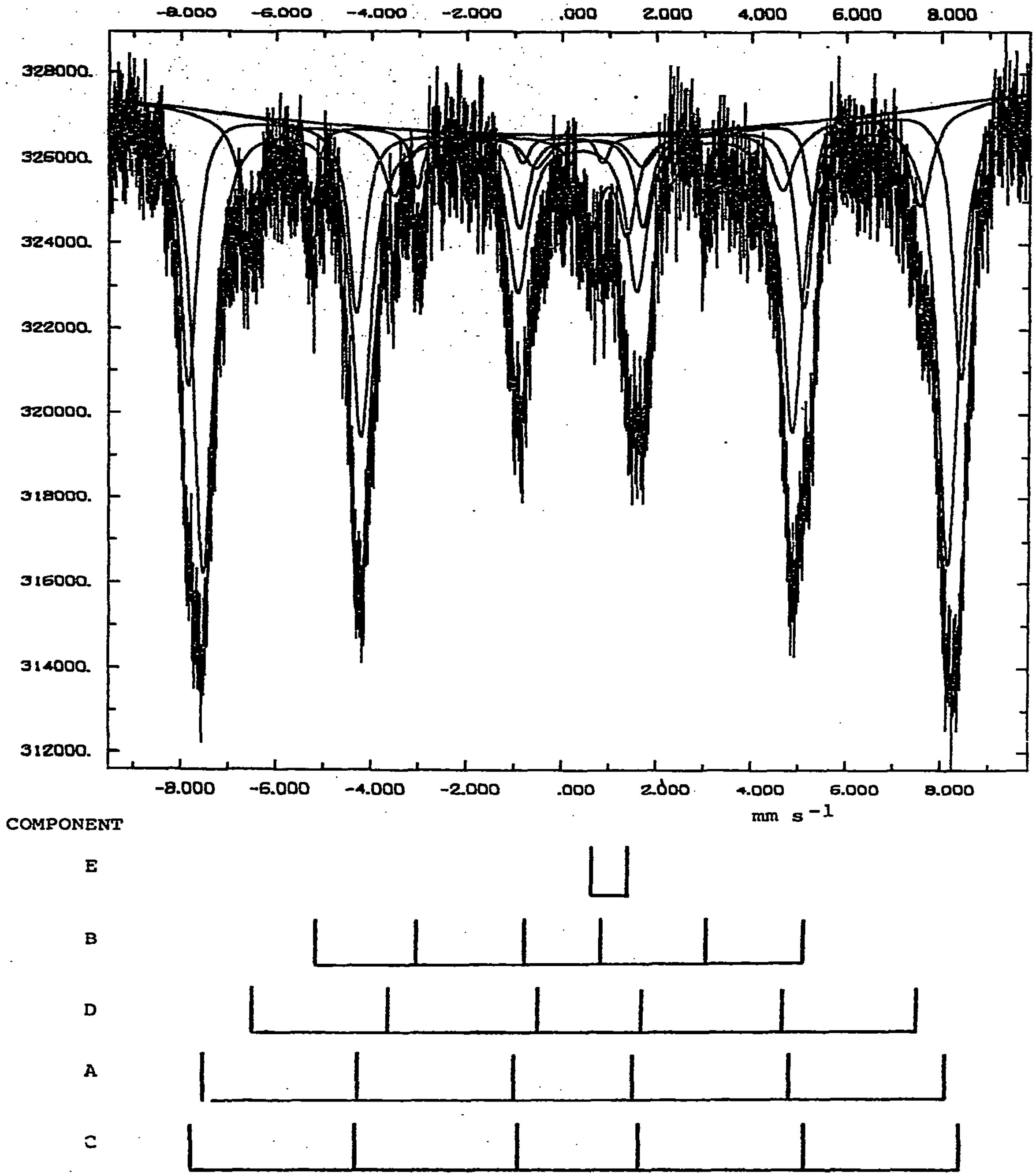

Fig. 1. Computer fitted room temperature Mössbauer spectrum of a sample fired to 700°C. χ^2 value 583.4 with 486 degrees of freedom. The componenets A—N in figs. 1—3 refer to Table 1.

even though the quadrupole splitting parameter is not in close agreement with the previously reported data which quote a value of 0.24 mm s^{-1} for 2ϵ.

The slightly lower values for both the internal magnetic field and the quadrupole splitting parameter may be due to the presence of impurities in the

TABLE 1

Room temperature Mössbauer results for samples fired to 700, 900 and 1100°C

Firing temp. (°C)	Component	δ ($mm\ s^{-1}$)	T ($mm\ s^{-1}$)	I (%)	H (kG)	2ϵ ($mm\ s^{-1}$)	ΔE ($mm\ s^{-1}$)	Comment
700	A	+0.306 ± 0.004	0.509 ± 0.023	51.9 ± 5.3	488.6 ± 0.6	+0.019 ± 0.009		γ-Fe_2O_3
	B	+0.002 ± 0.014	0.293 ± 0.034	5.6 ± 0.4	328.5 ± 0.9	0.000 ± 0.005		Fe metal
	C	+0.332 ± 0.005	0.409 ± 0.034	25.2 ± 3.0	507.2 ± 0.8	+0.119 ± 0.013		α-Fe_2O_3
	D	+0.521 ± 0.018	0.567 ± 0.068	12.3 ± 1.5	440.3 ± 1.8	+0.069 ± 0.034		Octahedral B site of Fe_3O_4
	E	+0.962 ± 0.021	0.467 ± 0.057	5.0 ± 0.4	0		0.766 ± 0.037	Non-stoichiometric ferrous oxide
900	F	+0.355 ± 0.005	0.329 ± 0.017	56.2 ± 2.4	514.5 ± 0.3	+0.217 ± 0.010		α-Fe_2O_3
	G	+0.163 ± 0.019	0.213 ± 0.067	8.1 ± 1.4	433.9 ± 1.1	−0.701 ± 0.039		Tetrahedral Fe(III) site of $Ca_2Fe_2O_5$
	H	+0.349 ± 0.008	0.229 ± 0.042	14.9 ± 1.6	0		0.263 ± 0.023	Fe(III)
	I	+0.354 ± 0.008	0.318 ± 0.038	21.8 ± 3.6	0		0.737 ± 0.033	Fe(III)
1100	J	+0.909 ± 0.023	0.585 ± 0.046	43.6 ± 5.7	0		0.909 ± 0.021	Non-stoichiometric ferrous oxide
	K	+1.180 ± 0.014	0.284 ± 0.069	9.8 ± 4.0	0		0.956 ± 0.025	Fe(II)
	L	+0.336 ± 0.017	0.452 ± 0.060	16.4 ± 1.6	504.8 ± 1.3	+0.632 ± 0.036		Octahedral Fe(III) site of $Ca_2Fe_2O_5$
	M	+0.140 ± 0.019	0.490 ± 0.064	17.0 ± 1.8	432.9 ± 1.3	−0.729 ± 0.038		Tetrahedral Fe(III) site of $Ca_2Fe_2O_5$
	N	+1.030 ± 0.011	0.381 ± 0.049	13.1 ± 2.2	0		1.933 ± 0.032	Fe(II)
$Ca_2Fe_2O_5$ as reported by Whitfield [8]		+0.335			514	+0.52		Octahedral Fe(III) site
		+0.185			437	−0.68		Tetrahedral Fe(III) site

crystal lattice. Component B, with an isomer shift of 0.0 mm s^{-1} and an internal magnetic field of 328.5 kG, is clearly due to the presence of unreacted iron metal ($\delta = 0.0$ mm s^{-1}, $H = 334$ kG) which is also confirmed by the absence of a quadrupole splitting. Two other components, labelled D and E in Table 1, remain. Component D has an internal magnetic field of 440.3 kG which corresponds closely with the literature value for the octahedral B site in Fe_3O_4 which has a magnetic field of 453 kG [7]. If component D is in fact due to the presence of Fe_3O_4 then another site is expected to be present due to the Fe(III) ions occupying the tetrahedral A sites in this compound. This would be expected to have a field value of about 491 kG and an intensity of about 0.5 times that of the B sites, i.e. an overall contribution of around 6% to the whole absorption spectrum. It is not possible to observe this due to the presence of components A and C which have a combined intensity of 77.1%; however, the presence of an unresolved site in this region would also help explain the large half width of component A, 0.509 mm s^{-1}. The large half width of component D is explained by the fact that this component is due to absorption by an octahedral site which is occupied by both Fe(II) and Fe(III) ions, electron hopping between adjacent sites giving an averaged spectrum at room temperature, which manifests itself in the form of unusually large line widths. Such line broadening is normally observed in room temperature spectra of samples of Fe_3O_4. Component E is assigned to a non-magnetically ordered site similar to that found in non-stoichiometric ferrous oxide. It is quite possible that under component E further peaks are present as suggested by the half width, 0.467 mm s^{-1}, but further resolution of the experimental data is not possible as the computer is already fitting 512 data points by 29 variable parameters. It should also be noted that the χ^2 value of 583.4 is quite acceptable for 486 degrees of freedom.

A dramatic change in the Mössbauer parameters of samples fired to 900°C was observed (Fig. 2). The best computer fit indicated that this spectrum consists of two quadrupole doublets and two sextets. The half widths of all four components were found to be below 0.340 mm s^{-1} and the χ^2 value of 533.4 falls well below the 0.1% level of 543.4 for 491 degrees of freedom; it is felt therefore that it is highly improbable that there are any unresolved components in this spectrum. Component F has a value for the internal magnetic field of 514.8 kG which is equal to the theoretical value of 515.0 kG for α-Fe_2O_3 at room temperature within experimental error. The isomer shift is close to the value reported for α-Fe_2O_3 (0.355 mm s^{-1} against 0.38 mm s^{-1} respectively [5]) and the value of the quadrupole splitting parameter +0.217 mm s^{-1} is in close agreement with the value of +0.24 mm s^{-1} quoted for pure α-Fe_2O_3. It is felt therefore that there is very strong evidence for the fact that component F is due to the presence of α-Fe_2O_3. Component G with a smaller isomer shift and a smaller value for the internal magnetic field is probably due to the presence of a tetrahedral iron site. In fact the isomer shift +0.163 mm s^{-1}, the quadrupole splitting parameter −0.701 mm s^{-1}, and the internal magnetic field parameter of 433.9 kG are all in close agreement with values reported by Whitfield [8] for the iron(III) tetrahedral site in $Ca_2Fe_2O_5$ [$\delta = +0.185$ mm s^{-1}, $\Delta = -0.68$ mm s^{-1} and $H = 437$ kG) (Table 1)]. However, there is no evidence in the present work to suggest the pres-

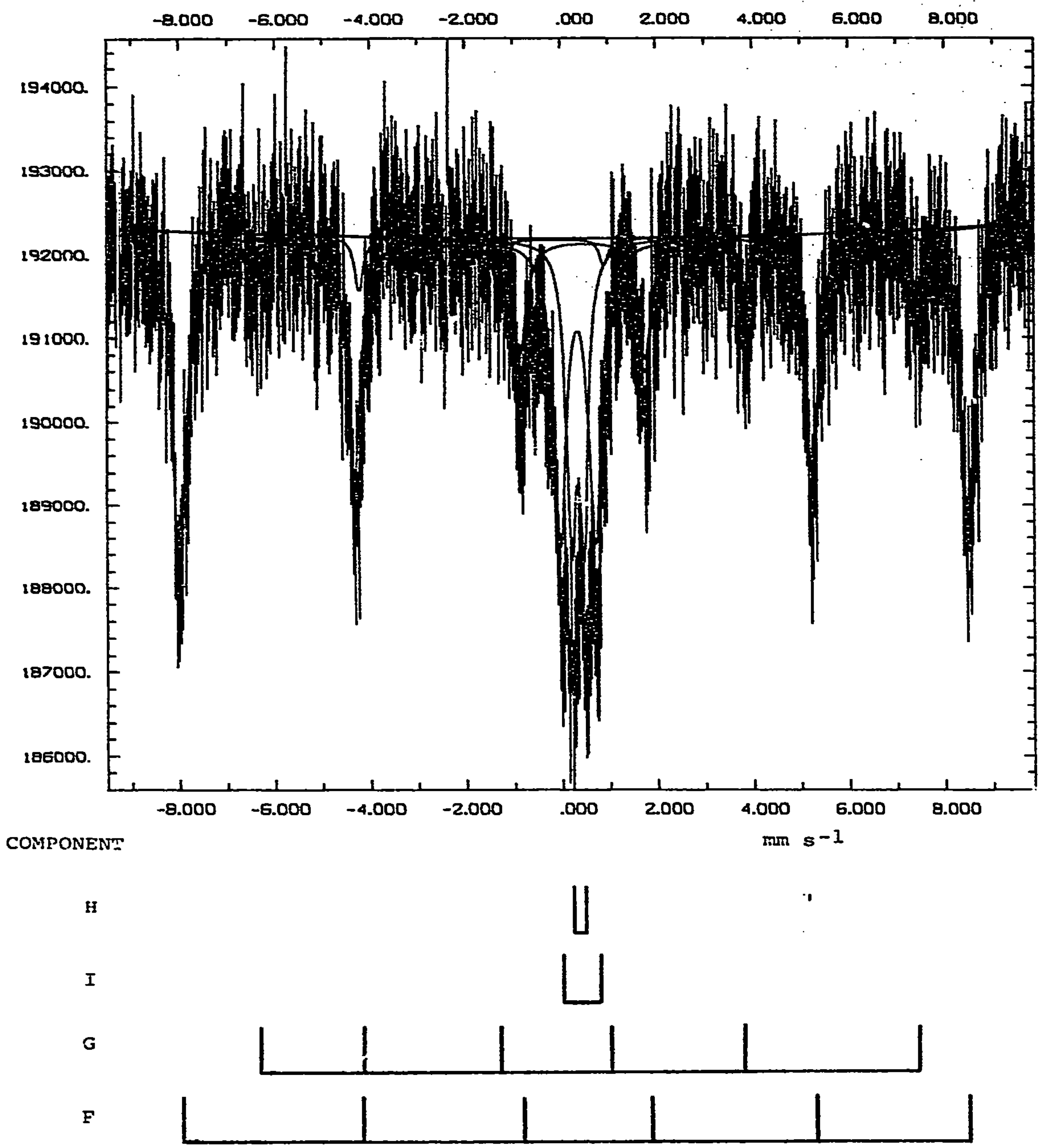

Fig. 2. Sample fired to 900°C. χ^2 value 533.4 with 491 degrees of freedom.

ence of the octahedral iron(III) site of this compound, in samples fired to 900°C.

This site, although having similar isomer shift and magnetic field parameters to α-Fe_2O_3, has been reported to have a quadrupole splitting parameter of +0.52 mm s^{-1}, which is significantly different from the value of +0.24 mm s^{-1} reported previously for α-Fe_2O_3 [5], and also does not coincide with any of the quadrupole splitting parameters found in the present work for samples fired to 900°C. Component H, with an isomer shift of +0.349 mm

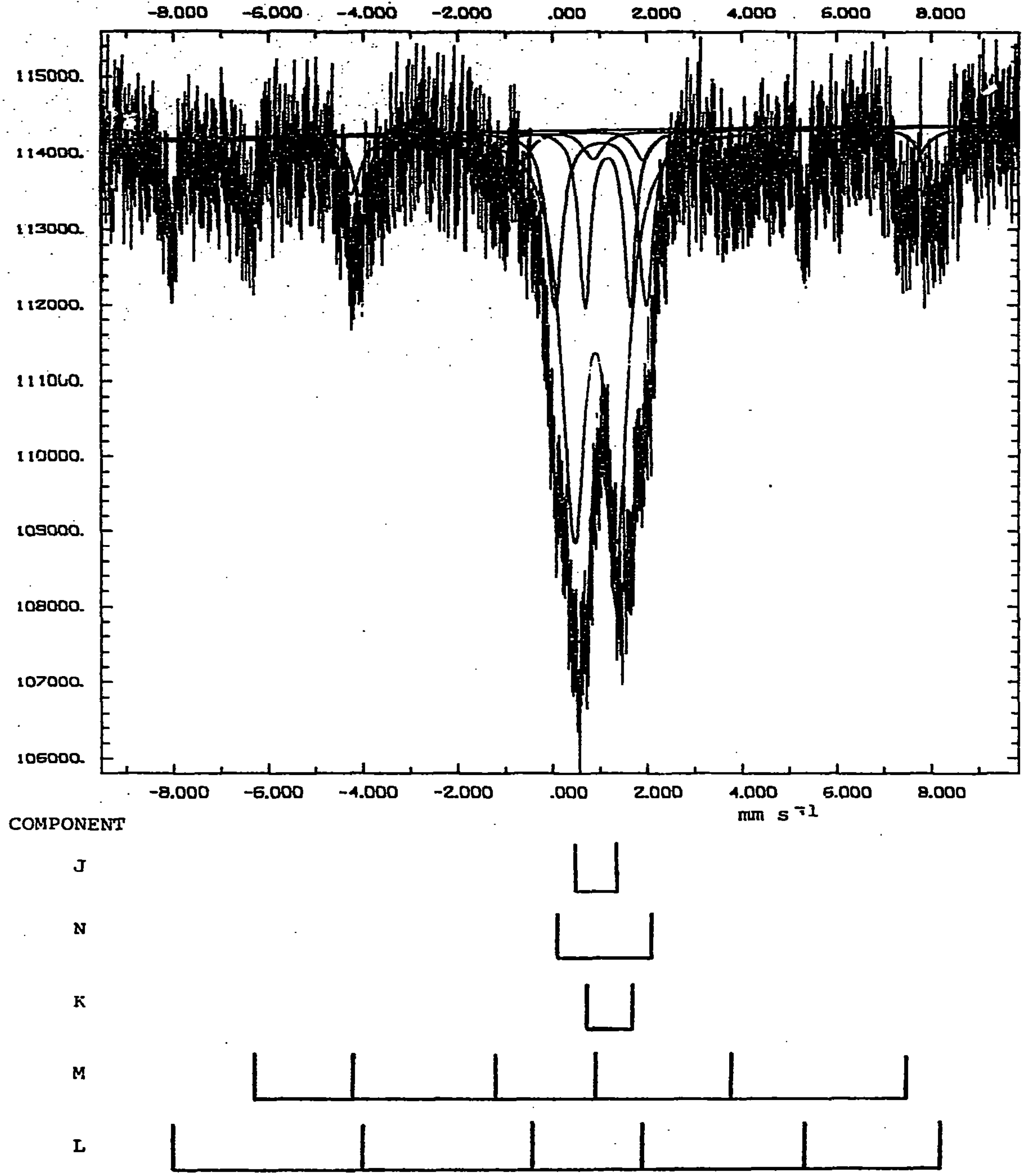

Fig. 3. Sample fired to 1100°C. χ^2 value 569.2 with 486 degrees of freedom.

s^{-1} and a quadrupole splitting of 0.263 mm s^{-1}, has parameters consistent with a non-magnetic iron(III) site. The quadrupole doublet I, having the same isomer shift within experimental error as the sextet F, could be due to the presence of super-paramagnetic particles of the latter. The fact that components F and I have appreciably larger line widths than components G and H tends to support this assumption. However, the similarity of the parameters of component F with those previously reported for pure α-Fe_2O_3 has already been mentioned but it should be noted that the quadrupole splitting of component I, 0.737 mm s^{-1}, is rather large for super-paramagnetic α-Fe_2O_3 so that the assignment of component I to a chemically known species is approached with caution.

On firing to 1100°C again an appreciable change in the Mössbauer spectrum is observed (Fig. 3). The best least squares computer fit indicates that two sextets and three doublets are present. The two sextets have parameters that are in good agreement with those previously reported by Whitfield [8] for $Ca_2Fe_2O_5$ (Table I). The three doublets all have parameters consistent with the presence of iron(II). There is not a very great difference between the isomer shifts of the three sites, the most intense component, J, having slightly the most negative value. This component also has a very large line width, 0.585 mm s^{-1}, indicating that it is probably made up of a number of components, hence it is suggested that this doublet is similar to the broad envelope reported previously for non-stoichiometric ferrous oxide [9]. Again it is not possible to further resolve this doublet as the maximum number of parameters are being used in the computer fit. The other two non-magnetic iron(II) sites, labelled K and N in Table 1, have much smaller line widths and it can be stated with greater certainty that these are both due to unique iron sites. It is tempting to suggest that, as the isomer shifts of these two sites are very nearly the same and as the quadrupole splitting of component K is approximately half that of component N, these two sites correspond to low spin iron(II) in *cis*- and *trans*-sites. It is felt, however, from evidence obtained from work on similar systems [1,10] that the oxygen anion ligand field is unlikely to be strong enough to stabilize low spin iron(II), so that although the above suggestion is kept in mind, in the absence of other structural information there is no evidence to support this and the quadrupole splitting ratio may simply be the result of a mathematical coincidence.

Chemistry

The Mössbauer evidence indicates that α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4 are all present in samples fired to 700°C. α-Fe_2O_3 has a corundum (α-Al_2O_3) type structure with a close-packed oxygen anion lattice within which the Fe(III) ions occupy octahedral holes [11]. γ-Fe_2O_3 and Fe_3O_4 both have spinel type structures of the form AB_2O_4, where the A ions are tetrahedrally co-ordinated and the B ions octahedrally co-ordinated to the oxygen anions [12]. There are insufficient Fe(III) ions in γ-Fe_2O_3 to fill all the B sites so that the exact stoichiometry corresponds to $Fe(A)(III)_{3/3} \cdot Fe(B)(III)_{5/3} \cdot X_{1/3} \cdot O_4$, where X is a cation vacancy in the B site lattice. Fe_3O_4 has exactly the same spinel structure as γ-Fe_2O_3 except that the B sites are completely filled by an equal number of Fe(III) and Fe(II) ions so that the stoichiometry corresponds to $Fe(A)(III)_{3/3} \cdot Fe(B)(III)_{3/3} \cdot Fe(B)(II)_{3/3} \cdot O_4$. It is interesting to note, bearing in mind the relationship between the structures of γ-Fe_2O_3 and Fe_3O_4, that the Mössbauer evidence suggests that the conversion of α-Fe_2O_3 to Fe_3O_4 under the present conditions could proceed via a γ-Fe_2O_3 intermediate. However, this is not conclusive, as it could well be that the result of a number of independant reactions is being observed. There is no guarantee that the α-Fe_2O_3 has to be converted to γ-Fe_2O_3 before it reacts with the iron metal to form Fe_3O_4 as it may just be that some conversion happens to take place before both the oxides are reduced. No calcium—iron containing species could be positively identified in samples fired to 700°C so it was not possible to obtain an insight into any possible role played by calcium in determining the chemistry of the system at this temperature.

There is quite strong Mössbauer evidence for the formation of $Ca_2Fe_2O_5$ in samples fired to 900°C as the parameters of the tetrahedral iron(III) site for this compound correspond closely with those of component G, although the octahedral site for this compound could not be observed. It is felt that there is no possibility of the octahedral site being obscured by the presence of α-Fe_2O_3 in this sample, for although the two species have similar isomer shift and magnetic hyperfine parameters, the difference between their quadrupole splitting parameters (0.30 mm s^{-1}) is of the order of one line width and it should therefore be possible to resolve one in the presence of the other in all cases except when the intensity difference is very large. This is also supported by the fact that the χ^2 value for this spectrum falls well below the 0.1% value so that it would appear that the formation of $Ca_2Fe_2O_5$ proceeds by a mechanism whereby the tetrahedral iron(III) site is formed, from a Mössbauer point of view at least, before the octahedral iron(III) site. The two other sites in this spectrum correspond to non-magnetic iron(III) sites but their assignment to chemically known compounds is more difficult.

The most significant point to emerge from this is that there appears to be no non-magnetic iron(II) present in samples fired to 900°C. All the iron(II) present must therefore occupy magnetic sites that are indistinguishable from magnetic iron(III) sites, which would be the case for instance if all the iron(II) was present in a compound of mixed oxidation state. This is one of the few instances when Mössbauer spectroscopy is insensitive to the oxidation state of the individual components involved. The question then arises as to where the iron(II) cations are located. Component F has already been shown to have parameters that are in close agreement with those previously reported for pure α-Fe_2O_3 and it is felt that appreciable substitution of iron(III) by iron(II) is unlikely without in some way changing the Mössbauer parameters.

The X-ray crystal structure of $Ca_2Fe_2O_5$ has been determined by Bertaut et al. [13] who showed that the average octahedral iron(III)—oxygen anion inter-ionic distance is 1.965 Å which is exactly equal, within experimental error, to the sum of the ionic radii of the two species concerned (i.e. 1.97 Å) if it is assumed that high spin iron(III) has a radius of 0.65 Å and that oxygen has an ionic radius of 1.32 Å as reported by Pauling [14]. On the other hand, the average tetrahedral iron(III)—oxygen anion distance for $Ca_2Fe_2O_5$ was reported by X-ray diffraction to be 1.865 Å, which is significantly smaller than the sum of the ionic radii for the two species involved (1.97 Å). The shorter distance can be explained by covalency effects, something which incidentally is confirmed by the smaller isomer shift of the tetrahedral iron(III) sites. If it is assumed, as stated above, that all iron(II) present in samples fired to 900°C occupy magnetic sites in which they are indistinguishable from the Mössbauer point of view from some iron(III) sites, then it is reasonable to expect that the iron(II) ions, which have a high spin ionic radius of 0.77 Å and therefore a sum of ionic radii of 2.09 Å with oxygen, would prefer to occupy an octahedral hole (radius 1.965 Å) rather than a tetrahedral hole (radius 1.865 Å). It is suggested that such preferential substitution of the octahedral iron(III) site occurs, therefore, in the present system and that electronic exchange between the iron(II) and the iron(III) octahedral sites is responsible for line broadening to such an extent that this site is rendered unobservable.

Whitfield [8] has reported the magnetic properties of $Ca_2Fe_2O_5$ together with a series of aluminium substituted ferrites. The aluminium cations are reported to substitute preferentially into the tetrahedral iron(III) sites. All the compounds studied were found to be antiferromagnetic, but a two-sublattice model, where the spins on the octahedral and tetrahedral lattices are opposed, was rejected on the grounds that although it correctly predicted antiferromagnetism for $Ca_2Fe_2O_5$, it predicted ferromagnetism for $Ca_2Fe_{3/2}$-$Al_{1/2}O_5$, in which there would be a residue of non-coupled paramagnetic sites in the octahedral lattice. This was in disagreement with both the Mössbauer results and the magnetic susceptibility results so that a four parallel sublattice model was proposed by Whitfield for this series of calcium ferrites in which both the octahedral and the tetrahedral lattices are composed of two sublattices, each of which has an equal number of oppositely aligned spins, so that the net magnetization of each sublattice remains zero and is independent of substitution by another cation. The substitution in the octahedral lattice of iron(III) by iron(II) in $Ca_2Fe_2O_5$ as reported in the present work is totally consistent with this model, as the Mössbauer parameters indicate that although such substitution greatly affects the spectral parameters of the octahedral sites, it in no way affects those of the tetrahedral sites, the magnetic properties of which are totally independent of those of the former.

Both the octahedral and the tetrahedral iron(III) sites of $Ca_2Fe_2O_5$ were resolved in samples fired to 1100°C. The intensity ratio of 1 : 1, within experimental error being the same as that reported by Whitfield indicating that all of the iron(II) that was present in the octahedral sites in samples fired to 900°C was oxidized to iron(III) on firing to 1100°C. $Ca_2Fe_2O_5$, which incidentally accounts for approximately one-third of the total iron present assuming that all the recoil free fractions are the same, appears to be the only iron(III) containing species in samples that have been fired to 1100°C. Nearly 50% of the total iron content is thought to be present as non-stoichiometric iron(II) oxide whilst the remaining 20% has been assigned, in equal ratios within experimental error, to two unique iron(II) sites. As the Mössbauer parameters do not coincide with any previously reported parameters for either iron oxide or calcium iron oxide systems, it is difficult to make any positive assignment for these two sites. The isomer shift of component N (Table 1) 1.030 ± 0.011 mm s^{-1}, agrees within experimental error to the value obtained when firing iron metal and haematite in an inert atmosphere together with a typical stoneware ceramic glaze recipe as previously reported [1], but the quadrupole splittings are quite different, 1.933 ± 0.032 mm s^{-1} compared to 2.36 ± 0.03 mm s^{-1}, suggesting that although chemically the environments may be similar, which is to be expected as in both cases the environment is composed of an octahedral array of oxygen anions, there is significant difference in the symmetries of the two iron(II) sites and therefore in the structure of the species involved.

CONCLUSION

The chemistry of the system studied in the present investigation is clearly complex. A number of iron oxides have been shown to be present in samples fired to 700°C although it is not possible to be precise about the exact nature or the number of reactions that occur. The co-existence of Fe_3O_4 and γ-Fe_2O_3 is of interest considering the close relationship between their structures. No evidence of any calcium—iron containing species could be found in samples that had been fired to this temperature. In samples fired to 900°C there is strong evidence for the presence of a calcium—iron oxide species similar in structure to $Ca_2Fe_2O_5$ but in which iron(II) is present to a certain extent in the octahedral iron(III) lattice. Such preferential substitution has been shown to be feasible sterically, and the Mössbauer results, which indicate that it has no effect on the tetradedral iron(III) parameters, are consistent with the behaviour expected for a species exhibiting four parallel sublattice antiferromagnetism as previously proposed by Whitfield for $Ca_2Fe_2O_5$ and a series of aluminium substituted derivatives.

It was in no way possible to speculate on the exact stoichiometry of the observed species from Mössbauer spectroscopy alone. In samples fired to 1100°C the iron(II) component of this compound was found to have oxidized and the spectral parameters reported in the present work are in close agreement with those previously reported for $Ca_2Fe_2O_5$. At least three non-magnetic iron(II) sites are present in samples fired to 1100°C but none can be assigned to chemically known species. Also none of these could be said to be similar to the unique site that was reported when equal stoichiometric amounts of iron metal and haematite were fired to 1100°C with ceramic glaze raw materials in proportions similar to a typical stoneware glaze recipe. It is concluded therefore that the unique site found in this system is not simply formed due to the interaction of the two iron containing species with calcium carbonate. It is felt that a lot of interesting chemistry occurs in this system which is now known to be more complex than was previously believed, so that a much fuller investigation of all the possible interactions will have to be undertaken before any firm conclusions can be made as to the relative importance of the different substituents in determining the final chemical environment of the iron(II) cations in stoneware type glaze systems.

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