

Mössbauer spectroscopic study of the decomposition mechanism of ankerite in CO₂ atmosphere

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Abstract

Mössbauer spectroscopy has been used to identify the iron-containing products that are formed during the thermal decomposition of ankerite in a CO₂ atmosphere. The decomposition takes place in three stages and evidence is produced to show that the first stage involves decomposition of ankerite to yield a periclase-wüstite solid solution, (Mg,Fe)O, along with calcite and CO₂, the periclase-wüstite then reacting with CO₂ to produce magnesioferrite (MgFe₂O₄) and CO. In the second stage the magnesioferrite and calcite react to produce periclase and dicalcium ferrite. The third stage does not involve reaction of Fe-containing phases and corresponds to the decomposition of calcite to CaO.

KEYWORDS: ankerite, decomposition, Mössbauer spectroscopy, CO₂ atmosphere.

Introduction

THE thermal decomposition of minerals of the dolomite-ankerite series has been described by Milodowski and Morgan (1981), who used a flowing CO₂ atmosphere (Warne *et al.*, 1981) to define the reactions clearly. Over the temperature range 500–1000 °C in a CO₂ atmosphere, decomposition occurs in three stages with the liberation of CO₂. The first two reactions also involve evolution of CO. With the iron-rich ankerite the first reaction leads to the formation of a spinel-type phase with XRD patterns consistent with the presence of either magnetite (Fe₃O₄) or magnesioferrite (MgFe₂O₄) together with periclase (MgO) and calcite (CaCO₃). Magnesioferrite was also identified by Conradi and Holth (1954) as one of the products formed on heating ankerite in air. In the second reaction, Milodowski and Morgan (1981) proposed that dicalcium ferrite (Ca₂Fe₂O₅) and magnesium oxide were formed by reaction of magnesioferrite with CaCO₃ and the third reaction was assumed to be the result of the decomposition of any previously unreacted CaCO₃.

In order to gain further insight into the nature of these decomposition processes, Mössbauer spectroscopic measurements have been performed on samples that had been heated to each of the three decomposition stages. Mössbauer

spectroscopy is a technique that is extremely sensitive to the chemical environment of iron, enabling both oxidation state and coordination number to be determined (see e.g. Bancroft, 1973; Goodman, 1980, 1981; Hawthorne, 1988). It therefore has the potential for characterizing the iron-containing phases at various stages in the decomposition of the ankerite.

Experimental procedures

The ankerite used in the present work originated from Erzberg, Austria, and was obtained from the BGS Reserve Collection (Ludlam collection, 29915). The ankerite was checked for purity by X-ray diffraction analysis (XRD) and characterized chemically. The composition was found to be Ca_{1.025}Mg_{0.329}Fe_{0.588}Mn_{0.060}(CO₃)₂. Trace amounts of free iron oxide (goethite) and quartz were found to be present.

Decomposition residues of this ankerite were prepared in two different experimental set-ups. 10 mg of powdered ankerite (less than 240 mesh BSS) were heated in flowing CO₂ to the end (approximately) of each of the three weight losses (Fig. 1a) using a Stanton Redcroft TG-770 microthermobalance. At the desired point during decomposition (monitored by the thermogravimetric (TG) curve) the power to the furnace was

switched off and the samples allowed to cool under the flowing CO_2 atmosphere. Residues were isolated from 740–750°C, 900–910°C and 1000°C. A second set of residues (Fig. 1*b*) was also obtained by heating the ankerite to the end of each reaction as monitored by simultaneous differential thermal analysis-evolved gas analysis (DTA-EGA) in a CO_2 atmosphere using a much larger sample (100 mg) in the apparatus described by Morgan (1977). A heating rate of 15°C/minute was employed in both TG and DTA-EGA apparatus. Although the DTA-EGA system produced much larger residues of ankerite, the system could not be quenched as rapidly as the TG apparatus since it relied solely on the natural cooling rate of the DTA furnace, whereas the TG furnace was water cooled. Therefore residues from the DTA-EGA equipment may have continued to decompose slightly during cooling.

The TG residues were characterized by X-ray

powder photography using Debye-Scherrer powder cameras. Spindles were prepared by rolling powdered residues with 'Durofix' cement and elemental Si was used as an internal standard. Photographs were recorded using $\text{Cu-K}\alpha$ radiation. The larger samples from the DTA-EGA apparatus were also characterized by X-ray diffractometry, again with elemental Si being used as an internal standard.

Mössbauer experiments were performed on a conventional constant acceleration spectrometer in transmission geometry with a source of ^{57}Co in Pd of nominal strength 25 mCi (0.93 GBq). Measurements were made at ambient temperatures (295–300 K) and at the boiling point of liquid nitrogen (*c.* 77 K), the latter in a bath-type cryostat. Spectra were fitted to a number of doublets (components having equal areas and widths) by a computer program which assumed Lorentzian shape for all peaks. Isomer shifts of the various

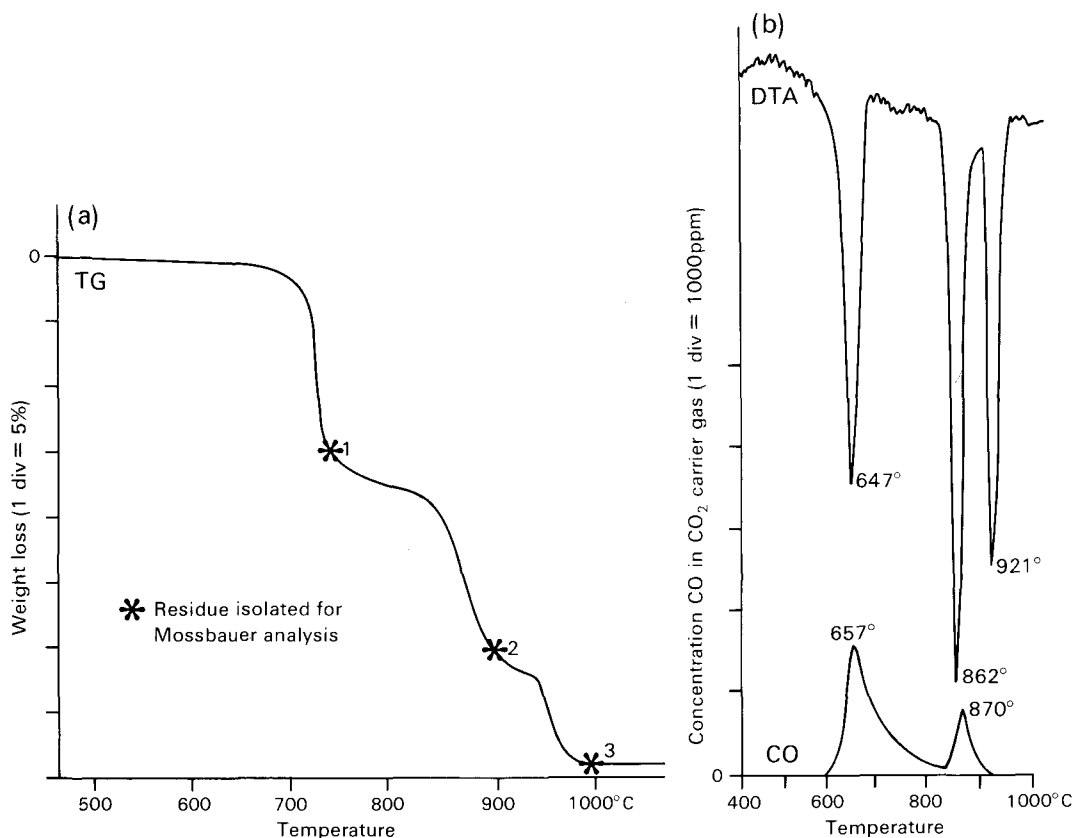


FIG. 1. TG (a) and simultaneous DTA-EGA (CO), (b) curves for ankerite, $\text{Ca}_{1.025}\text{Mg}_{0.329}\text{Fe}_{0.588}\text{Mn}_{0.060}(\text{CO}_3)_2$ showing the pattern of decomposition in flowing CO_2 atmosphere (redrawn from data of Milodowski and Morgan, 1981).

species are presented relative to iron metal, which was used as a calibration standard.

Results and discussion

The thermal decomposition of ankerite occurs in three distinct stages (Fig. 1) and XRD data for the products formed on heating to each of the peaks were identical to those represented by Milodowski and Morgan (1981). Thus the 1st reaction yielded a spinel-type phase with spacings consistent with either magnetite (Fe_3O_4) or magnesioferrite (MgFe_2O_4), periclase (MgO) and calcite (CaCO_3). The samples from the 2nd and 3rd reactions gave patterns consistent with dicalcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$), calcite and periclase, with the calcite lines being significantly weaker after the 3rd reaction. A small amount of quartz, which is present as an impurity in the original ankerite, was seen in all of the samples.

Mössbauer spectra of the same samples at ambient temperature and 77 K are shown in Figs 2 and 3 along with spectra of the unaltered ankerite, and computed parameters for the constituent species are given in Table 1. The spectra of the unaltered ankerite show clearly that all of the iron is in the Fe(II) form with parameters typical of those reported in the literature for iron(II) carbonate minerals (Stevens *et al.*, 1983). No evidence is seen for any other iron-containing phases in the mineral.

After heating, the results show that all of the iron is in the Fe(III) form, with the exception of the samples heated to the first decomposition peak where approximately 15% remains as Fe(II) in the sample produced in the TG apparatus (Figs 2*b*, 3*b*). The sample produced in the EGA apparatus had only about 5% Fe(II) but was otherwise identical with that from the TG apparatus. The quadruple splittings for the Fe(II) in these samples at both room temperature and 77 K are quite different from those of the ankerite, indicating that this component does not represent a small amount of unaltered ankerite. All of the Fe(III) species exhibit magnetic structure at both ambient temperature and 77 K, which demonstrates that these are iron-rich phases in which the magnetic ordering temperature is well above 300 K. The magnitudes of the magnetic fields and isomer shifts are also consistent with the iron being present in oxide environments (Murad and Johnston, 1987).

The Mössbauer results show definitively that the product formed after the first decomposition reaction is not magnetite. This is because magnetite has a very distinct Mössbauer spectrum as a result of the distribution of equal amounts of

Fe(III) in the tetrahedral and octahedral sites and Fe(II) in the octahedral sites of the inverse spinel structure. Above the Vervey transition at *c.* 120 K (Vervey *et al.*, 1947) there is rapid electron hopping between the octahedrally coordinated Fe(II) and Fe(III) with the result that the spectrum has two distinct magnetically-ordered components, one with isomer shift consistent with tetrahedral Fe(III) and the other, with approximately twice the intensity, having isomer shift intermediate between Fe(II) and Fe(III) in octahedral coordination (Bauminger *et al.*, 1961). There is, however, no component in Figs 2*b* or 3*b* with such an isomer shift, nor indeed with parameters consistent with any magnetically-ordered Fe(II). Only one sextet is resolved in the spectra, but the asymmetry in the intensities of the high- and low-velocity peaks in the spectrum at 77 K indicates that more than one structural environment exists. The isomer shift is rather low for octahedral coordination in oxides and it is likely that this spectrum contains a contribution from tetrahedral Fe(III), although the presence of such a component cannot be conclusively established. It is worth noting that maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which is a non-stoichiometric spinel having approximately one site in nine vacant, has a spectrum (Bauminger *et al.*, 1961) with a similar shape to that of the heated ankerite, thus lending support for the spectrum originating from a combination of octahedral and tetrahedrally-coordinated Fe(III). Also, there is only a small quadruple splitting term in this spectrum and the asymmetric line intensities could alternatively be explained by the existence of a small range of magnetic fields and quadruple splittings in the sample. Sawatzky *et al.* (1969) report that spectra of MgFe_2O_4 at 77 K and above cannot be analysed in detail because of a large amount of overlap between the A- and B-site ions. Thus in view of the XRD findings it is likely that MgFe_2O_4 is the major species formed after the first decomposition reaction.

After the second reaction, two Fe(III) components are clearly present in the Mössbauer spectra and can be assigned, on the basis of the magnitudes of the isomer shifts, to occupancy by Fe(III) of sites with octahedral and tetrahedral coordination. In contrast to the product formed after the first reaction, both components exhibit large quadruple splittings, these being negative for the octahedral site and positive for the tetrahedral site (Table 1). It is because of this difference in sign that the two components are so clearly resolved in the Mössbauer spectra. Similar spectra are observed after the third reaction, thus supporting the conclusions of Milodowski and Morgan (1981) that this last reaction corresponds to

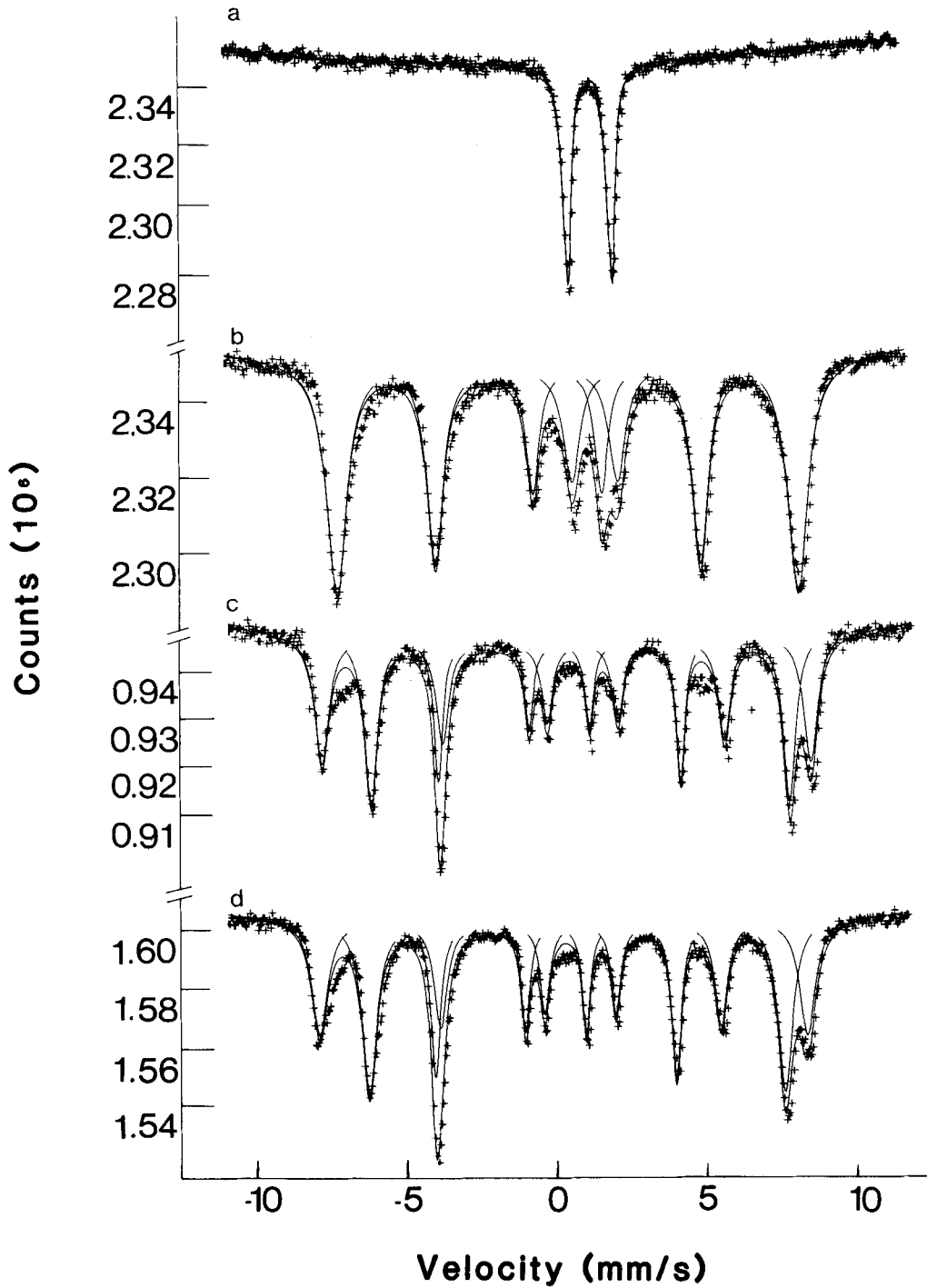


FIG. 2. Mössbauer spectra at ambient temperature of ankerite (a) unheated and after heating to (b) 740°C, (c) 910°C and (d) 1000°C in CO₂ in TG apparatus. Solid lines illustrate the individual peaks and envelopes from the computer fits to the data.

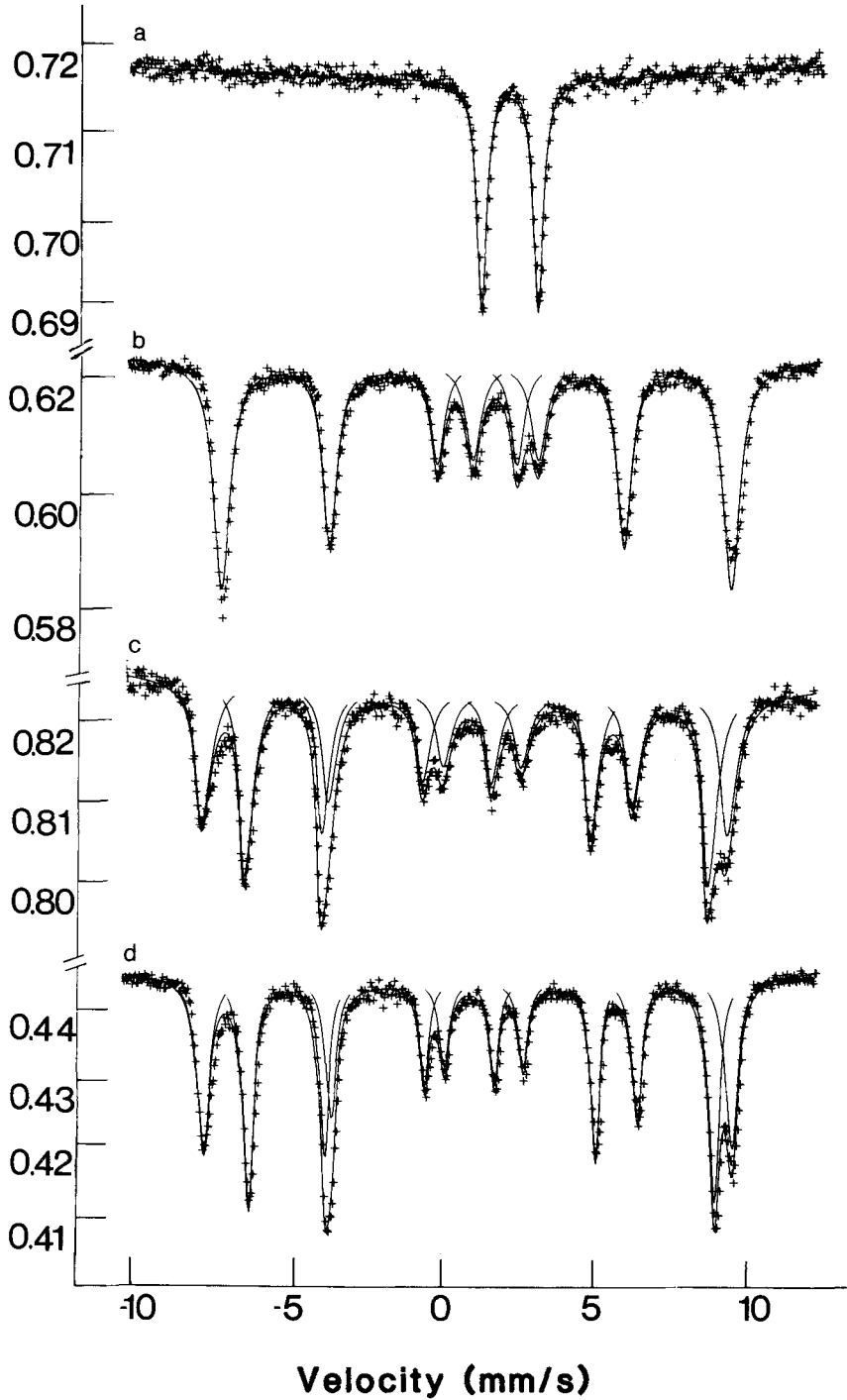


FIG. 3. Mössbauer spectra at 77K of ankerite (a) unheated and after heating to (b) 740°C, (c) 910°C and (d) 1000°C in CO₂ in TG apparatus. Solid lines illustrate the individual peaks and envelopes from the computer fits to the data.

Table 1 Computed parameters from the Mössbauer spectra of ankerite, unheated and heated to near the end of each of its three decomposition temperatures

		Fe(II)			Fe(III)			
		δ^a	Δ^a	% ^c	δ^a	ϵ^a	B ^b	% ^c
Unheated	RT ^d	1.236	1.438	100		----		
	77K	1.357	1.843	100		----		
Heated to temp. (i)	RT	1.215	1.521	17	0.305	-0.005	47.4	84
	77K	1.352	2.125	16	0.417	-0.009	51.5	84
Heated to temp. (ii)	RT				(0.343	-0.278	50.3	50
					(0.176	+0.346	43.1	50
	77K				(0.435	-0.226	53.6	58
					(0.271	0.336	47.7	42
Heated to temp. (iii)	RT				(0.358	-0.287	50.1	45
					(0.176	+0.355	42.9	55
	77K				(0.452	-0.269	53.1	47
					(0.277	+0.345	46.9	53

a δ , Δ and ϵ in mm/s; δ relative to Fe metal

b B in Tesla

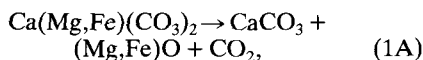
c percentage contribution to total absorption area

Errors on δ , Δ , and ϵ are better than ± 0.010 , B is ca. ± 0.5 and % is ca. ± 2

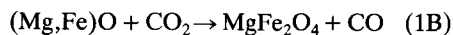
d RT = room temperature

decomposition of CaCO_3 and does not involve any Fe-containing species. The magnitudes of B_{hf} for the octahedral and tetrahedral components are similar to those reported by Akiyama (1981) for $\text{Ca}_2\text{Mn}_x\text{Fe}_{2-x}\text{O}_5$ and support the assignment of the XRD results to $\text{Ca}_2\text{Fe}_2\text{O}_5$.

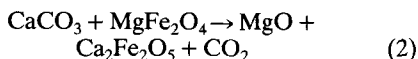
In the light of these Mössbauer results, it is possible to refine the decomposition process for the ankerite, bearing in mind that the existence of calcite and periclase had already been established as products of the first reaction and dicalcium ferrite and periclase were present after the second reaction. The initial reaction, therefore, probably involves demixing of the solid solution, followed by breakdown of the iron and magnesium components, according to the reaction:



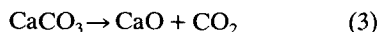
with some of the CO_2 oxidizing the iron according to the reaction



In the second reaction calcite and magnesioferrite react to produce dicalcium ferrite:



and the third reaction involves decomposition of calcite:



The Fe(II) that is seen in the Mössbauer spectra after the first reaction is probably unreacted $(\text{Mg,Fe})\text{O}$. It is almost certainly not in the magnesioferrite, where the Fe(III) is completely

ordered and there is no evidence for any Fe(II) in the same structure. The presence of some unreacted $(\text{Mg,Fe})\text{O}$ after the first DTA peak also explains the evolution of some CO during the second reaction, since reaction (1B) will be occurring simultaneously with reaction (2).

Conclusions

The use of Mössbauer spectroscopy to study the decomposition residues of ankerite in a CO_2 atmosphere has helped to refine earlier decomposition mechanisms proposed on the basis of thermal analysis and X-ray diffraction studies. These earlier studies showed that ankerite decomposes in three stages. The first stage involves decomposition of the ankerite to produce calcite, periclase and a spinel-like phase (either magnetite or magnesioferrite) with the evolution of CO_2 and CO. XRD data are unable to distinguish between magnetite or magnesioferrite. However, the Mössbauer spectra are consistent only with the formation of magnesioferrite, not magnetite, as a reaction product. The Mössbauer spectra also indicate the presence of unreacted $(\text{Mg,Fe})\text{O}$ (periclase-wustite solid solution), which suggests that two simultaneous reactions occur during the first stage. The first reaction is the dissociation of the ankerite into CaCO_3 , $(\text{Mg,Fe})\text{O}$ and CO_2 . The second reaction involves rapid oxidation of $(\text{Mg,Fe})\text{O}$ to MgFe_2O_4 , liberating MgO and evolving CO.

Mössbauer data for the residue from the second decomposition step confirm earlier results and are consistent with the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ by solid-state reaction of CaCO_3 and MgFe_2O_4 . The

Mössbauer results also show that no Fe-bearing phase is involved during the final decomposition step, in which any remaining CaCO_3 dissociates to $\text{CaO} + \text{CO}_2$.

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