Mineralogical alteration of thermally treated siderite in air: Mössbauer spectroscopy results

PAN Yongxin[1], ZHU Rixiang[1] and PING Jueyun[2]

1. *Institute of Geophysics, Chinese Academy of Sciences, Beijing* 100101, *China*;
2. *Department of Materials Physics, Beijing University of Science and Technology, Beijing* 100083, *China*

Abstract Mineralogical alternation of thermally treated siderite in air atmosphere has been systematically analyzed by Mössbauer effects. It was preliminarily estimated from the area of subspectra that 4%, 39% and 62% of magnetite were formed at 410℃, 490℃ and 510℃ respectively. After being incrementally heated at 530℃ the spectra consist of two sextets of Fe_3O_4. Sextet of γ-Fe_2O_3 with hyperfine field of 50T was observed at 550℃. Spectra at 580℃ consisted of two sextets with hyperfine fields caused by γ-Fe_2O_3 and α-Fe_2O_3. Fe_3O_4 disappeared and the amount of γ-Fe_2O_3 decreased, while the quantity of α-Fe_2O_3 increased to 34% and 77% at 640℃ and 690℃, respectively. During the early stage of decomposition and oxidation, FeO was probably produced but quickly oxidized to magnetite and unidentified in our experiment. These results, in good agreement with the X-ray diffraction analyses and microscopic observation, provide an interpretation to anomalous magnetic property changes of siderite-bearing rock samples.

Keywords: siderite, mineralogical phase transition, thermally treated in air.

THERMAL decomposition and oxidation of the mineral siderite, $FeCO_3$, has been a topic of considerable interest for many years because of both its commercial importance and scientific questions regarding the progression of products. Siderite is one of the common minerals in sediments deposited in anoxic environments. X-ray diffraction (XRD) and Mössbauer effect were used to study the nature of unheated siderite[1,2]. Thermal decomposition kinetics of siderite[3] and decomposition in room-temperature ball milling[4] were also studied. Gallagher *et al*. reported the decomposition of siderite in vacuum, nitrogen and O_2, respectively[5, 6].

Anomalous magnetic properties of siderite-bearing rocks have been noticed by many paleomagnetists[7—9]. The temperature-dependence of both magnetic susceptibility and anisotropy of magnetic susceptibility (AMS) had been revealed in our previous rock-magnetic investigations[10]. It was also revealed that siderite likely transformed to ferrimagnetic minerals created a very strong secondary chemico-viscous remanent magnetization. In this case, false interpretation to paleomagnetic data may be made. Nevertheless, the mechanism that links the magnetic properties and the mineral transition in air atmosphere are poorly understood today. In this note we report a preliminary result of Mössbauer specstropy for products of siderite thermally treated in air and its interpretation for rock magnetic properties.

1 Experimental methods

Samples studied were collected from Dalizi Iron Deposit, Jilin Province. X-ray fluorescence (XRF) and thin section inspection showed that samples consist of high purity crystalline siderite. In the laboratory thermally treated samples were incrementally heated in air in a modern MMTD 60 thermal demagnetiser (Magnetic Measurements) at intervals of 50—10℃ up to 680℃ (keeping for 40 min at each hold interval). The thermal treating temperature in this note refers to the highest temperature to the specific specimen except for specification. Susceptibilities and AMS were determined on a KLY-3s spinner Kappabridge. XRD and remanent magnetization measurements were conducted at the JICA Centre of CAS and Paleomagnetism Laboratory of the IG-CAS. Thermomagnetic balance analysis was made at the Tectonophysics Laboratory of the Chinese Seismic Bureau.

Mössbauer effect analyses were conducted in the Mössbauer Spectroscopy Laboratory at the Beijing University of Science and Technology. The samples were ground into powder, then homogeneously mixed with pure vacuum grease to prevent oxidation. The thicknesses were about 10 mg iron per cm^2. Mössbauer spectra were taken by a conventional constant-acceleration spectrometer with 25mCi^{57}Co(Pd) source at room temperature. The experimental velocities were calibrated with an α-Fe standard spectrum. The data of counts were folded to increase the ratio of signal to noise. All spectra were fitted with Lorentzian line shape using a least-square method.

2 Results and discussion

Susceptibility measurements showed that susceptibilities of siderite-bearing samples had a strong temperature-dependence[10]. On incrementally heating, siderite was clearly with paramagnetic characteristics until 250℃, decreasing with temperature enhancement. Between 400—510℃ the susceptibility increased sharply and reached a peak value at 510—530℃, indicating formation of some new magnetic mineral phase. A sharp drop took place between 540—570℃, likely representing the Curie temperature of magnetite. A similar variation pattern was observed in thermomagnetic analysis.

Select pure natural crystalline siderite and heat incrementally in air at temperatures of 410, 490, 510, 530, 580, 640 and 680℃. Samples were sealed in plastic bags after cooling to room temperature to prevent from possible further oxidization. Mössbauer effect experiments at room temperature were instantly carried out. Results are shown in table 1 and figure 1.

An important act for Mössbauer specstropy to siderite is that all Fe^{2+} sites are equivalent[11]. Fig. 1 shows that the Mössbauer spectrum of siderite at room temperature was characteristic of a paramagnetic doublet with isomer shift of 1.2 mm/s and quadrupole splitting of 1.8 mm/s, similar to result of Gil *et al*.[2]. After being heated at 410℃ an admixture of the quadrupole doublet of $FeCO_3$ with magnetically split components of Fe_3O_4 were detected. Further increase of the treatment temperature resulted in a

Table 1 Mössbauer parameters and interpretation of siderite phase transition at different temperature

Temperature/℃	I.S./mm·s^{-1}	Q.S./mm·s^{-1}	B_{hf}/T	Area (%)	Mineral phase
15	1.230	1.796	0.0	100.0	$FeCO_3$
410	1.228	1.793	0.0	94.0	$FeCO_3$
	0.561	0.029	45.14	0.4	Fe_3O_4(site B)
	0.442	-0.121	49.45	5.6	Fe_3O_4(site A)
490	1.225	1.787	0.0	50.6	$FeCO_3$
	0.561	0.029	45.15	11.6	Fe_3O_4(site B)
	0.323	-0.010	49.43	37.8	Fe_3O_4(site A)
510	1.231	1.788	0.0	28.6	$FeCO_3$
	0.570	-0.032	45.43	17.5	Fe_3O_4(site B)
	0.333	-0.019	49.46	53.9	Fe_3O_4(site A)
530	0.569	-0.033	45.67	22.3	Fe_3O_4(site B)
	0.327	-0.000	49.37	77.7	Fe_3O_4(site A)
580	0.569	-0.033	45.67	4.1	Fe_3O_4(site B)
	0.321	0.008	48.80	29.5	Fe_3O_4(site A)
	0.385	-0.089	50.74	46.8	γFe_2O_3
	0.374	-0.090	51.61	19.6	αFe_2O_3
640	0.315	0.000	48.97	66.0	γFe_2O_3
	0.379	-0.090	51.22	34.0	αFe_2O_3
680	0.320	-0.012	49.47	22.6	γFe_2O_3
	0.378	-0.102	51.38	77.4	αFe_2O_3

I.S., Q.S., and B_{hf} refer to isomer shift, quadrupole splitting and hyperfine field, respectively.

decrease in area of doublet and increase in one of sextets. If f factor is equal for each site, the area of subspectrum was directly proportional to the number of iron nucleus at a site. It can be estimated from the area of subspectra that 4%, 39% and 62% of magnetite are formed at 410, 490 and 510℃ respectively. After a treatment at 530℃ the spectra consisted of two sextets with hyperfine field of 49T and 45T correspondent to iron atoms at site A (Fe^{3+}) and site B (Fe^{3+} and Fe^{2+}) of Fe_3O_4, which is of spinel structure and belongs to the cubic crystal system. Because of a quick exchange between electrons of Fe^{3+} and Fe^{2+} on site B, sextets on site B were overlapped to one another. Sextet of γ-Fe_2O_3 with hyperfine field of 50T could be observed after being heated at 550℃. Spectra at 580℃ consist of two sextets with hyperfine fields caused by γ-Fe_2O_3 and α-Fe_2O_3. After that, Fe_3O_4 disappeared and the amount of γ-Fe_2O_3 decreased, while the quantity of α-Fe_2O_3 increased. It reached 34% and 77% approximately when the samples were treated at 640 and 690℃, respectively. Compared with XRD and microscopic observations, it is found that they are in good agreement and provide an good interpretation to magnetic property changes of siderite samples.

Identification of the mineralogical alteration of siderite is very important for the following two reasons. Siderite is a common constituent in sedimentary rocks deposited in lake, deep-sea and other anoxic environments. On the other hand, secondary magnetization caused by the oxidation of siderite either by laboratory thermo-treatments or by natural geological heat event influences seriously the magnetic properties and their implications of paleoenvironmental/paleomagnetic data. Gallagher *et al*. reported that hematite was the sole product when siderite oxidized in oxygen atmosphere[6]. In nitrogen ambient, iron metal and magnetite were formed when siderite was heated to 385 and 410℃. At the higher temperatures, 450 and 600℃, the decomposition of siderite was almost complete and the wüstite and magnetite predominated[12]. Seguin studied the rate of dissociation and the problem of stability of siderite in air and concluded that the solid end product was always αFe_2O_3, the life of transitional phase was believed to be the order of a fraction of a second[13]. Bagin and Rybak and Loseva found that heating of siderite above 300℃ might form magnetite and maghemite, and hematite as an end product at complete oxidation[14,15]. This study demonstrates that both spinel-structural magnetite and maghemite are intermediate products

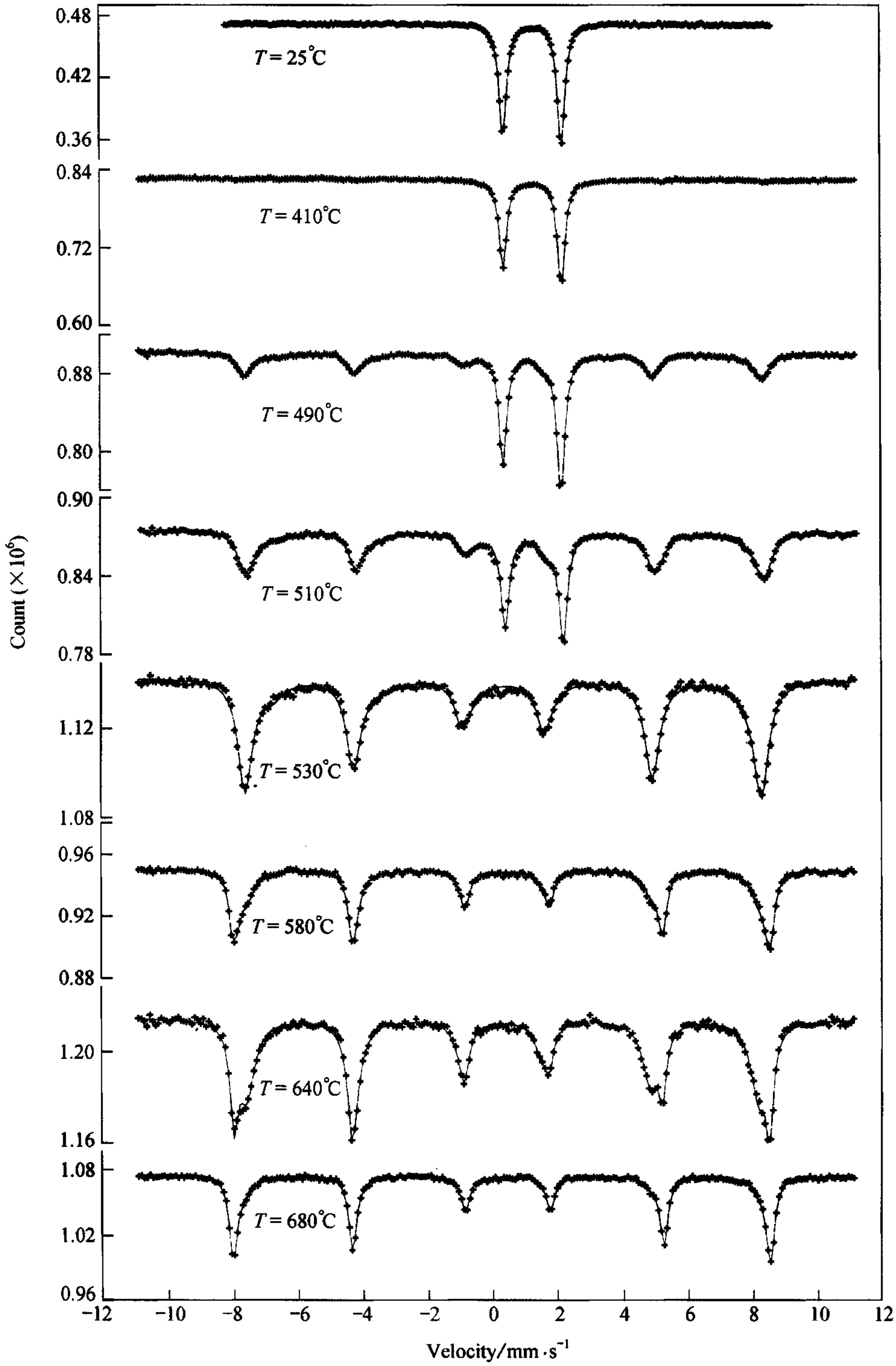

Fig. 1. Mössbauer spectroscopy at room temperature of heated samples in air.

with relative stability to some extent. Magnetite might be decomposed from siderite mineral directly, or produced by oxidation reaction between FeO and carbon oxide gas. FeO is not found in our experiments. XRD results proved that spinel structural magnetite and maghemite are dominant products (fig. 2) when siderite was heated to 720℃ consecutively in air atmosphere. M(T) curve also shows that magnetite occurs with a clear 580℃ Curie temperature.

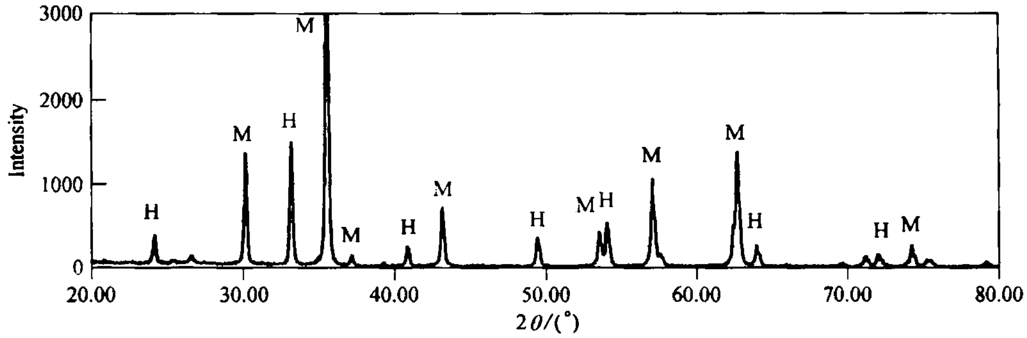

Fig. 2. XRD result for a sample heated consecutively up to 720℃. H, Hematite; M, spinel-structural magnetite and maghemite.

3 Conclusions

In thermally treated siderite in air atmospere both magnetite and maghemite are intermediate products and relatively stable to some extent. At 680℃, hematite, the final product, is dominant in the product with some maghemite mixture.

Processes of decomposition and oxidization of siderite heated in air might be expressed as follows: $3FeCO_3 \rightarrow Fe_3O_4 + 2CO_2 + CO$; $4Fe_3O_4 + O_2 \rightarrow 3\gamma Fe_2O_3 + 3\alpha Fe_2O_3$. An intermediate reaction process $FeCO_3 \rightarrow FeO + CO_2$; $3FeO + CO_2 \rightarrow Fe_3O_4 + CO$ may occur at the early stage. FeO is probably oxidized quickly and unidentified in Mössbauer effect results.

Mineralogical phase transition processes revealed in our experiment explicate variations of susceptibility and AMS of siderite-bearing rock in thermal demagnetization. Clearly, those secondary magnetic minerals can produce a strong visco-chemical remanent magnetization in rocks. If one hopes to enhance AMS or separate the characteristic remanent magnetization (ChRM) from the lake and marine sediments in which mineral siderite existed as either a detritus mineral or matrix mineral through a thermal treatment, caution should be taken.

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