



High temperature behavior of iron carbonates: an in-situ Mössbauer study

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Abstract

The thermal decomposition of four iron carbonates (siderites) and their decomposition products in a vacuum ($\sim 2 \cdot 10^{-5}$ Pa) was investigated for the first time using in-situ transmission ^{57}Fe Mössbauer spectroscopy. These measurements were supported by X-ray diffraction, X-ray fluorescence, Raman spectroscopy, magnetic measurements, and transmission electron microscopy. Mössbauer spectra were collected from room temperature (RT) to 750 °C, and the sample was then cooled to RT. The initial samples contained siderite as the only Fe-mineral, and its content in the analyzed samples was greater than 80%. Heated samples contained hematite and magnetite as the only Fe-bearing phases. Siderite decomposition occurs in the temperature range of 300–500 °C. The analysis shows that iron carbonates transform directly into magnetite. Then hematite generation occurs as long as siderite is present in the sample because, during its decomposition, oxygen is produced, which enables the oxidation of Fe^{2+} ions in magnetite and the formation of hematite. Changes in hyperfine parameters, such as isomer shift, quadrupole splitting, and hyperfine magnetic field, as a function of temperature were obtained for iron carbonates and iron oxides (hematite, magnetite). These results have not yet been published and allow the identification of iron carbonates and iron oxides in other materials exposed to high temperatures. The measurements also show that magnetite formed during the decomposition of siderite consists of particles of various sizes with a low degree of crystallization.

Keywords Iron-bearing carbonate · Siderite · Thermal decomposition · Hematite · Mössbauer spectroscopy

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Introduction

The carbon exchange between the Earth's interior and the surface occurs over time scales of billions of years and constitutes the geodynamical carbon cycle (Boulard et al. 2012). Carbon is recycled through subduction into the deep Earth, mainly as carbonates (Boulard et al. 2012; Liu et al. 2019). Two types of rhombohedral carbonates – the calcite group and the dolomite group – together constitute the most abundant carbonate minerals in the Earth's crust, along with calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) (Hazen et al. 2013). Among the most important carbonate minerals belonging to the calcite group are calcite, magnesite (MgCO_3), rhodocrosite (MnCO_3), and siderite (FeCO_3) (Hazen et al. 2013; Martin et al. 2017). Siderite is an iron-bearing carbonate mineral common in oxygen-free environmental conditions, including lakes, rivers, and marine sediments (Isambert et al. 2003; Halas and Chlebowski 2004; Dideriksen et al. 2015; Koo and Kim 2020). Natural siderites often contain significant substitutions of Mg, Ca, and Mn for Fe in the lattice (Fisher et al. 1998; Dideriksen et al. 2015), and pure siderite is seldom found. Siderite crystallizes in the trigonal crystal system and is rhombohedral in shape, typically with curved and striated faces, and the color of siderite ranges from yellow to dark brown or black, the latter being due to the presence of manganese (Ponomar et al. 2017). This carbonate is an important mineral that finds application in various industries and has gained commercial importance over the years (Koshy et al. 2018); for example, it is one of the primary sources of iron in Europe (Binder et al. 1981), in petroleum drilling fluids as a scavenger for H_2S and in processes for making ferrous catalyst materials (Abou Alfa et al. 2019; Mohamed et al. 2020; Kruszewski and Ciesielczuk 2020) or in the combustion of the coast (Zhang et al. 2017).

The thermal decomposition of iron carbonates is significant because of the industrial relevance of this mineral (Song et al. 2014; Zhu et al. 2023). The mechanism of this process depends on their composition and experimental conditions like temperature, atmosphere, or sample microstructure. Many studies have been carried out on the mechanism of thermal decomposition of siderite in the air atmosphere using, for example, thermomagnetometry and thermogravimetry (Fisher et al. 1998; Isambert et al. 2003; Zhu et al. 2023) or X-ray diffraction analysis (Isambert et al. 2003; Song et al. 2014). As they show, the final product of the thermal decomposition of siderite in an air atmosphere is hematite ($\alpha\text{-Fe}_2\text{O}_3$). The final product decomposition of FeCO_3 was Fe_3O_4 in a CO_2 atmosphere (Shunzo 1966; Song et al. 2014) while the FeO and Fe_3O_4 were only observed in an inert atmosphere or a vacuum (Shunzo 1966; Song et al. 2014; Wang et al. 2015; Koshy et al. 2018; Zhu et al. 2023).

The studies mentioned above were concentrated mainly on the final products of the thermal decomposition of siderite under different conditions. The process of thermal decomposition of siderite (Gallagher and Warne 1981; Gotor et al. 2000; Feng et al. 2011) and the products of this transformation under various external conditions are relatively well-described. Still, only limited work has been performed in-situ on this thermal reaction process.

In this work, the iron carbonates high-temperature decomposition and products of this process in a vacuum ($\sim 2 \cdot 10^{-5}$ Pa) were characterized using an in-situ ^{57}Fe Mössbauer spectroscopy (nuclear resonance technique). This technique is very sensitive to the local atomic structure, its local deformation, and atomic or lattice defects when treating the Fe nucleus as a probe of its local surroundings. Based on the results of this method, we obtain information about the iron oxidation states, the local iron microenvironments, the iron magnetic states, and the relative fractions of iron-bearing components (De Grave et al. 1999; Bianchi et al. 2021). The results of our measurements not only describe the siderite decomposition process but also show the high-temperature behavior of iron oxides formed in this process. Changing hyperfine parameters like isomer shift, quadrupole splitting, or hyperfine magnetic field versus temperature were obtained for siderite and its decomposition products (hematite, magnetite). Such results were presented for the first time and can be used to identify siderite and iron oxides obtained in various high-temperature processes, e.g., metallurgical processes. The Mössbauer investigation was supported by magnetic measurement, X-ray diffraction, X-ray fluorescence, transmission electron microscopy, and Raman spectroscopy.

Materials and methods

Various carbonate rocks are present in the Upper Silesian Coal Basin, Poland. These are mainly siderites in the form of sphaerosiderites, shoal siderites, and carbonaceous siderites. The studied siderites come from coal seams from Ruda Bed's upper parts, in the Chwałowice Trough's eastern part, in the Upper Silesian Coal Basin. Siderites in the seams occurred in claystone layers, forming intergrowths with a thickness of 0.10 to 0.80 m. Macroscopically, siderite is gray or dark grey, sometimes with a beige tinge. The texture is usually massive and chaotic, sometimes directional, and poorly marked due to thin carbon laminae ~ 0.5 mm thick. The rocks are cut with carbonate veins 0.5–5 mm thick. A detailed description of the investigated materials has been previously described in the literature (Kądziołka-Gaweł et al. 2023). The research was carried out on four rock samples taken from different seams. These samples were designated Sd1, Sd2, Sd4 and Sd5.

X-ray fluorescence

The chemical composition is reported as oxide contents (wt%) following standard X-ray fluorescence (XRF) practice with a ZSX Primus II Rigaku spectrometer. The spectrometer, equipped with the 4 kW, 60 kV Rh anode and wavelength dispersion detection system, allowed for the analysis of the elements from Be to U. No external standards were necessary. Only the internal standards coupled with the fundamental parameters were implemented. Sample preparation for XRF elemental analysis requires a smooth and uniform sample surface. Therefore, the powdered samples were pressed in a specialized laboratory hydraulic press to obtain tablets form. Total iron is expressed as FeO^T . Carbon and loss on ignition (LOI) were not determined; therefore, analytical totals below 100 wt% reflect mainly carbonate-bound CO_2 and, to a lesser extent, structurally bound H_2O associated with clay minerals.

X-ray diffraction

Minerals present in the raw siderite samples and after annealing at 750 °C were determined using X-ray diffraction (XRD) method. These studies were performed on powdered samples using a Siemens D5000 X-ray diffractometer ($\text{CuK}\alpha$ radiation, Ni filter). Rietveld refinement was performed in a licensed X'Pert High Score Plus with a PDF-4 crystallography database. The percentages of individual components in initial samples were determined using the Rietveld method. The content of a given phase should be greater than 2% by volume. It is then assumed that the phase is correctly identified. The crystal (crystalline) sizes of iron oxides in the annealed samples were estimated using the Scherrer equation (Muniz et al. 2016), which relates the diffraction line width to crystallite size. The crystallites size was determined for the reflections originating from the planes (104) for Fe_2O_3 and (311) for Fe_3O_4 , which are occurring at angles of 33.19° and 30.21°, respectively.

Magnetic measurements

The magnetic measurements of the investigated samples were made in the temperature range of ~100 – 800 °C by the Faraday method using electronic microbalances with automatic compensation and in the magnetic field of 1.2 T. The sample chamber was maintained at a constant vacuum 10^{-2} Pa. The sample was heated at 10 °C/min and cooled at 5 °C/min. Based on these results, the Curie temperatures (T_C) and Neel temperature (T_N) for all magnetically ordered phases were determined based on the first derivative of the magnetization with respect to temperature (dM/dT).

Mössbauer spectroscopy

The ^{57}Fe Mössbauer transmission spectra were recorded at room and high temperatures using an Integrated Mössbauer Spectroscopy Measurement System (designed by Waław Musiał and Jacek Marzec, Poland), and a source ^{57}Co : Rh (25 mCi). A gas proportional counter LND-45431 was used as a gamma-ray detector. The spectrometer velocity scale was calibrated at room temperature with a 25 μm thick $\alpha\text{-Fe}$ foil. Data was collected with a 1024-channel analyzer (before folding). All Mössbauer measurements were carried out on powdered samples, and the Mössbauer absorber was placed in a boron nitride container in a vacuum oven. During temperature measurements, the interior of the furnace was evacuated using a vacuum pump (HiCube 80 Eco, Germany), and the vacuum in the experimental chamber was approximately $2 \cdot 10^{-5}$ Pa. The amount of the sample was chosen to get a thickness of ~8 mg Fe/cm^2 . The sample temperature was controlled with an accuracy of 0.1 °C. Temperature measurements were made in steps of 50 °C, starting from 50 °C up to 750 °C, and then the sample was cooled down to room temperature with steps 100 °C. The sample was heated and cooled at 5 °C/min. Each high-temperature measurement took ~12 h. This time was the optimal time to obtain spectra with good statistics. The Mössbauer spectra were evaluated by least-square fitting of the lines using the MossWinn4.0i program. The spectral parameters such as isomer shift (IS), quadrupole splitting (QS), quadrupole shift for magnetically split spectra (ϵ), magnetic hyperfine field (B), full line width at half maximum (Γ), and relative subspectrum area (A_{rel}) were determined. Relative areas of spectral components determine relative quantification of phase composition. The isomer shifts are given relative to $\alpha\text{-Fe}$ at room temperature. Some parts of the spectra were fitted with a hyperfine magnetic field distribution. The model and implementation are based on the Voigt-based fitting method (Rancourt and Ping 1991). What is more, parameters of the Mössbauer spectra like center shift (CS) or quadrupole splitting (QS) may provide information regarding the lattice dynamics (Podgórna et al. 2017; Scrimshire et al. 2018). The center shift (CS), which is the location of the centroid of Mössbauer peaks in velocity relative to a standard ($\alpha\text{-Fe}$ in our case), has two components: the isomer shift (IS), and the second-order Doppler shift (SOD) (Podgórna et al. 2017; Scrimshire et al. 2018):

$$CS(T) = IS + SOD(T) \quad (1)$$

The changes of CS with temperature are mainly due to second-order Doppler shift (SOD), while isomer shift (IS), also called chemical shift, is practically temperature independent. SOD is related to the atomic mean square displacement and

for this reason is strongly temperature dependent (Podgórna et al. 2017; Scrimshire et al. 2018):

$$SOD = -\frac{3k\theta_D}{2Mc} \left[\frac{3}{8} + 3 \left(\frac{T}{\theta_D} \right)^4 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \right] \quad (2)$$

where c – velocity of light, k – Boltzmann constant, M is the mass of the iron, taken as 57 Da (multiplied by Avogadro's constant for conversion to mass), and θ_D is the Debye temperature. Based on the temperature dependencies of the above-mentioned quantities, the Debye temperature was estimated for siderite.

Raman spectroscopy

Structural characterization of siderite degradation products performed using a WITec confocal Raman microscope CRM alpha 300R. A solid-state laser ($\lambda = 532$ nm, $P = 5$ mW) was coupled to the microscope through a single-mode optical fiber with a 50 μm diameter. The laser radiation was focused onto the sample via an air Olympus MPLAN (100x/0.76NA) objective, while the scattered light passed through a multi-mode fiber (100 μm diameter). The powder material was placed under the objective lens. The sample was lightly “pressed” using glass slides to obtain a relatively flat surface to avoid secondary scattering from surface irregularities and grain edge effects. The laser beam struck the sample at 90° , and, in the same geometry, the scattered signal was collected by the same objective lens. Raman spectra were gathered using 20 scans with an integration time of 20 s and a resolution of 3 cm^{-1} . The spectrometer monochromator working with a 600 line/mm grating was checked before the measurements using a silicon plate (520.7 cm^{-1}). A post-processing analysis, including cosmic ray removal and baseline correction, was performed in WITec Project Five Plus. Gauss-Lorentz band fitting analysis used the Grams 9.2 software package to estimate the real bands' position.

Transmission electron microscopy

The images of the structure and morphology of selected siderite samples were recorded with using a Titan 80–300 (FEI) S/TEM microscope at 300 kV. The analysis of TEM and especially HRTEM images provides information about the changing size of the nanoparticles forming different materials and their crystalline structure. Moreover, the crystallographic composition was analyzed using selected-area electron diffraction (SAED). Sample preparation for TEM analysis consisted of dispersing them in ethanol and then drop-casting onto lacey carbon-coated copper TEM grids.

Results

X-ray fluorescence

Table 1 presents the bulk chemical composition of the investigated raw siderite-bearing samples, determined by X-ray fluorescence (XRF) and reported as oxide contents. The data include only those components whose concentrations exceeded 0.05 wt%. The chemical composition reveals dominant amounts of iron ($\text{FeO}^T > 43\text{ wt}\%$), which, together with carbon and oxygen, constitutes the iron carbonate phase (FeCO_3). The presence of SiO_2 and Al_2O_3 , accompanied by minor amounts of K_2O and TiO_2 , reflects the occurrence of quartz and clay minerals (illite and kaolinite), as independently identified by X-ray diffraction method (XRD). These oxides do not originate from the siderite crystal structure itself but represent minor silicate impurities within the studied bulk samples. Magnesium and calcium oxides are mainly related to the presence of dolomite identified by XRD, whereas manganese is interpreted as partially replacing Fe^{2+} in the siderite structure.

X-ray diffraction

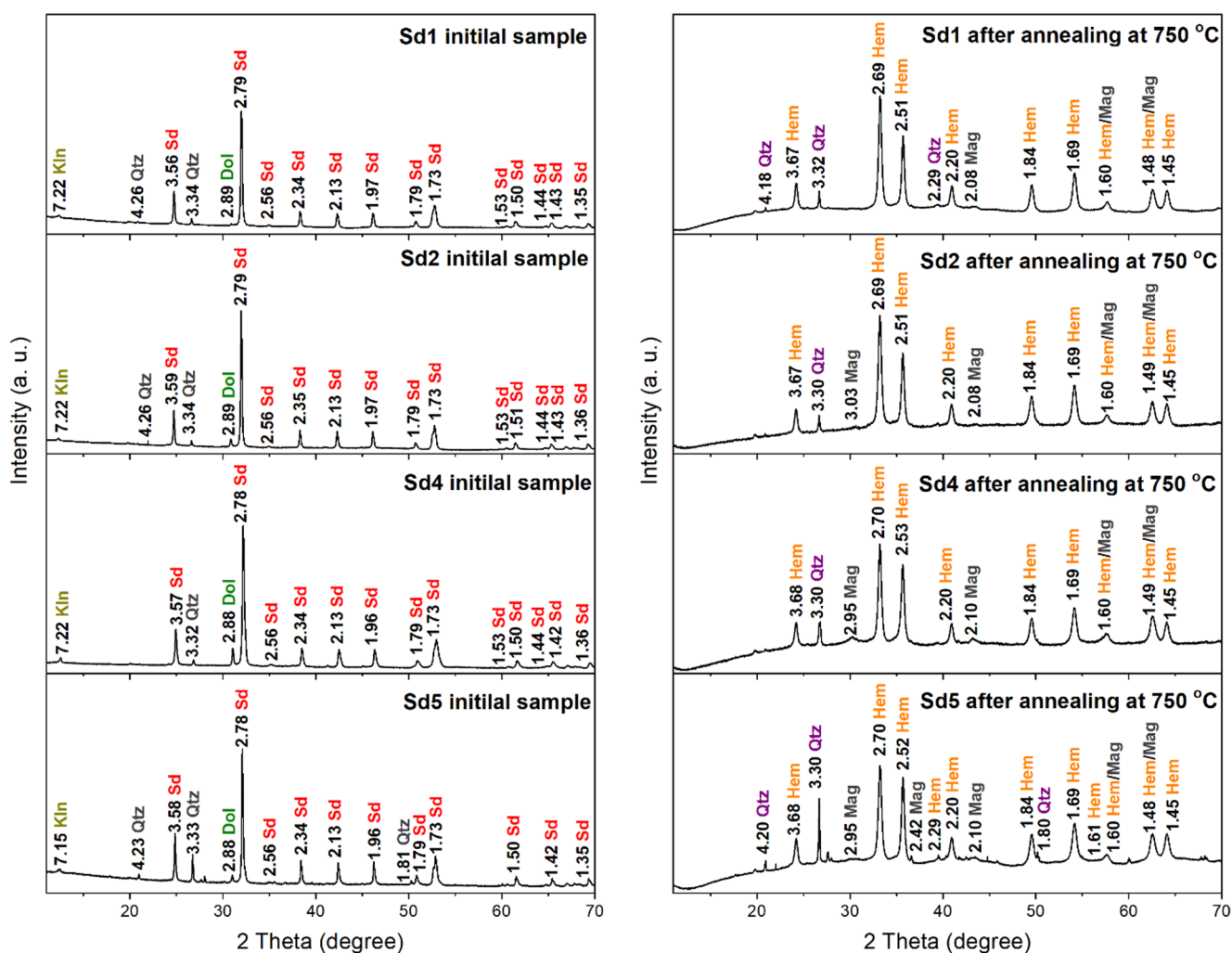
Measurements by XRD revealed that initial siderite samples contained siderite as the main component and small amounts of accessory minerals (Table 2; Fig. 1). A small

Table 1 Chemical composition (weight%) of the studied bulk siderite-bearing samples reported as oxide contents; total iron is expressed as FeO^T . Totals below 100 wt% result from the presence of carbonate-bound CO_2 and, to a lesser extent, structurally bound water associated with clay minerals

Sample	Chemical component (wt%)									
	FeO^T	MnO	MgO	CaO	K_2O	Al_2O_3	SiO_2	TiO_2	P_2O_5	Total
Sd1	44.97	0.77	1.33	1.20	0.39	4.97	9.80	0.15	0.39	63.97
Sd2	44.83	0.62	1.11	1.02	0.37	4.50	8.26	0.13	0.53	61.37
Sd4	43.13	0.75	2.60	2.56	0.30	4.10	7.36	0.13	0.37	61.30
Sd5	45.75	0.56	2.35	1.97	0.57	5.03	14.44	0.18	0.55	71.40

Table 2 Quantitative phase composition (wt%) of the investigated siderite samples before and after annealing at 750 °C, determined by X-ray diffraction and Rietveld refinement. Phases with contents below 1 wt% are reported as “<1” due to increased relative uncertainty near the detection limit. The estimated uncertainty is ± 2 wt% for major phases and ± 1 wt% for minor phases

	Component	Formula	Sample			
			Sd1	Sd2	Sd4	Sd5
Initial samples	Siderite	FeCO_3	94	90	86	79
	Quartz	SiO_2	<1	<1	<1	7
	Illite	$\text{K}_{0.65}\text{Al}_{2.0}[\text{Al}_{0.65}\text{Si}_{3.35}\text{O}_{10}](\text{OH})_2$	<1	<1	<1	<1
	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	5	2	<1	2
	Dolomite	$\text{CaMg}(\text{CO}_3)_2$	<1	6	13	11
Sum			99	98	99	99
Heated at 750 °C	Hematite	$\alpha\text{-Fe}_2\text{O}_3$	83	75	39	71
	Magnetite	Fe_3O_4	16	25	42	14
	Quartz	SiO_2	<1	<1	19	14
Sum			99	100	100	99

**Fig. 1** XRD patterns of the initial siderite samples and heat-treated up to 750 °C and cooled to room temperature. The interplanar spacing values are shown in the diffractograms. Sd—siderite, Kln—kaolinite, Dol—dolomite, Mag—magnetite, Hem—hematite, Qtz—quartz

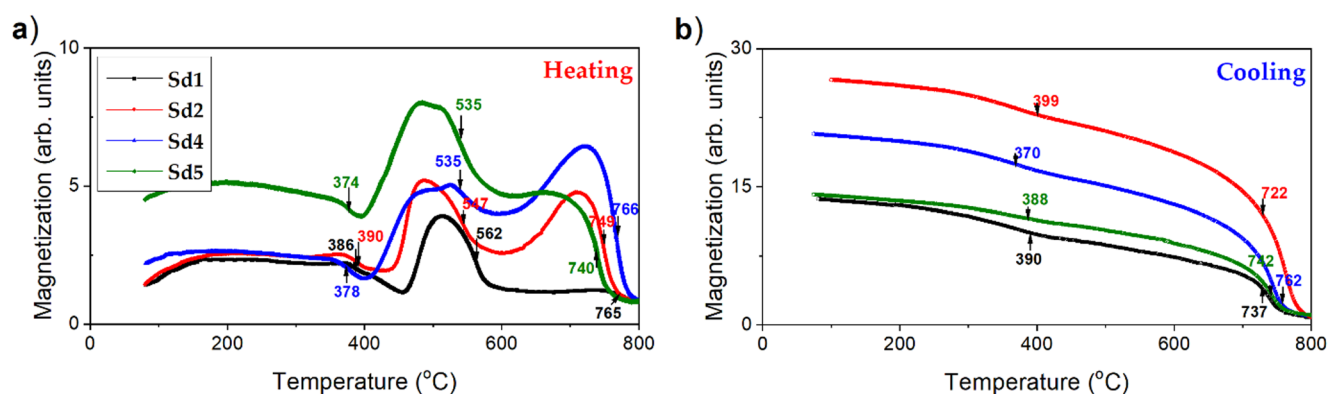


Fig. 2 Magnetization versus temperature (M-T) plots obtained during heating **a**) and cooling **b**) siderite samples Sd1, Sd2, Sd4, and Sd5. Black arrows indicate magnetic transition temperatures; the values of these temperatures (in °C) are given above the arrows

concentration of quartz, illite, and kaolinite were detected in all non-heated samples. In particular, samples Sd4 and Sd5 contain significant amounts of dolomite. The higher Mg and Ca contents in the elemental composition of these samples (Table 1) are likely due to the presence of this mineral. After heating the samples to 750 °C, and then cooling down to room temperature, hematite (α -Fe₂O₃) and magnetite (Fe₃O₄) are the only Fe-bearing phases in the samples (Table 2; Fig. 1). The highest concentration of α -Fe₂O₃ (~83%) was in the sample Sd1 and the smallest (~39%) in the sample Sd4 (Table 2). All samples after heating also contain quartz. The content of this silicate is quite significant, especially in samples Sd4 and Sd5. No C-containing substances are present in the diffraction patterns of the annealed samples. They are beyond the detection limit. The reflections associated with the Fe₃O₄ visible in the diffractograms (Fig. 1) are quite broad. Such wide lines may indicate a high disorder of this phase and/or small crystallite sizes. For annealed samples, the determined crystalline sizes of hematite are 24.5(2) nm for Sd1, 22.2(2) for Sd2, 22.5(2) for Sd4, and 21.2(2) for Sd5, respectively. In all the investigated samples, the hematite crystallite sizes obtained in this study are similar to those reported in the literature (Gwoździk 2018; Eneroth and Bender Koch 2003). The determined crystallite sizes for magnetite are 15(2) nm for Sd1, 26(4) nm for Sd2, 13(1) nm for Sd4, and 8(1) nm for Sd5. These magnetite crystallite sizes are significantly smaller than those determined for hematite, particularly for the Sd4 and Sd5 samples, and are like those observed for magnetite nanoparticles (Roca et al. 2007; Upadhyay et al. 2016).

Magnetic measurements

The temperature-dependent magnetization curves (M-T) of all the investigated siderites were measured during heating and cooling in an external magnetic field of 1.2 T, as shown in Fig. 2. Above temperature about 370 °C for all samples

Table 3 Magnetic properties of the siderite and the identified phases in Sd1, Sd2, Sd4, and Sd5 samples. Here, T_{Sd} is a siderite decomposition temperature, T_C is Curie temperature for magnetite and magnesio-magnetite, T_N is Neel temperature for hematite. The maximum error for the T_{Sd} , T_C , and T_N values was ± 5 °C; only for magnesio-magnetite was the maximum error in $T_C \pm 10$ °C

Temperature	Sample			
	Sd1	Sd2	Sd4	Sd5
Siderite decomposition T_{Sd} (°C)	386	390	378	374
Magnetite T_C (°C)	562	547	535	535
Magnesio-magnetite T_C (°C)	390	400	370	388
Hematite T_N (°C)	Heating	765	749	766
	Cooling	737	722	762

one can observe a small decrease in magnetization, which indicates decomposition temperature of the studied siderites (T_{Sd}). The exact values of this temperature for all samples are presented in Table 3. As can be seen, the values of these temperatures are slightly higher than those obtained for pure siderite (350 °C) (Garcia et al. 2012) and can be affected by partial substitution of Fe²⁺ in the cationic sublattice. An increase in magnetization is observed above 400 °C for all samples (Fig. 2), with a broad maximum for Sd1 and Sd2 samples, and double maximum for Sd4 and Sd5. Such an increase in magnetization with increasing temperature indicates the formation of new magnetic phase. The subsequent decrease in magnetization with increasing temperature suggests some magnetic transition, probably related to magnetite. The estimated values of this transition temperature (Table 3) are 562 °C for sample Sd1, 547 °C for Sd2, 535 °C for samples Sd4 and Sd5. These temperatures are slightly lower than those for bulk magnetite (583 °C) (Levy et al. 2012; Fabian et al. 2014). This may be because the Curie temperature decreases with decreasing particle size (Penny et al. 2019) and the substitution of iron ions by magnesium (Ponomar et al. 2017). The two additional transitions observed at temperature 493 °C for Sd4 and 487 °C for Sd5 sample may be related to poorly crystalline magnetite and

magnetite in which Mg ions substitute for Fe ions. After that, the magnetization slowly decreases with the increase in temperature, and the minimum is close to 800 °C. The magnetic transition temperatures were also calculated from these slopes (Fig. 2; Table 3) for increasing and decreasing temperatures. Such high temperatures can indicate the magnetic transition of hematite (680 °C) (Fabian et al. 2014) but obtained values are a bit too high (>700 °C) on this iron oxide. This effect can be explained based on the Dzialoshinskii theory (Aharqni et al. 1963; Moskvina 2021), which assumes that the temperature at which the basal plane anisotropy passes zero is shifted with the substitutions, and the transition at ~680 °C can be shifted considerably by partially substituting Cr, Al, Ga, or Mn for the iron in α -Fe₂O₃. Additionally, for this iron oxide, differences between the T_N values determined during heating and cooling (Table 3) of the sample are also visible. We interpret the observed T_N changes during these processes as related to the heterogeneity of the hematite grains, which could result from cation reorganization during heating. Additionally, for the siderite samples, Sd2 at temperature ~715 °C and Sd4 at ~730 °C are visible with some maxima on magnetization curves. This effect can be related to the decomposition of dolomite (Valverde et al. 2015), which is in higher amounts of these samples (Table 2). However, such a maximum was not observed for sample Sd5, where the concentration of dolomite is higher than in sample Sd2. For this reason, we can assume that this peak is likely Hopkinson-peak effects and was observed for hematite-containing samples (De Boer and Dekkers 1998; Muxworthy et al. 2023). Hopkinson peak is usually associated with the unblocking of single-domain grains, making them superparamagnetic or increased domain wall motion in larger multi-domain grains due to enhanced thermal energy; both mechanisms cause an increase in magnetization, though this is particularly enhanced in fine single-domain grains (Muxworthy et al. 2023). During cooling back to room temperature (RT), the plot shows that the magnetization values were not reversible with temperature. However, a characteristic “knee” appears on the M-T curve in the temperature range of about 300–450 °C, which indicates some magnetic transition in these samples. The exact temperatures of this transition are listed in Table 3. This transition is likely related to the magnetic transition in magnetite, where Mg replaces some of the Fe ions. In such a case, we can talk about Mg-rich magnetite, the so-called magnesio-magnetite, where magnetic transitions were observed in this temperature range for such type of compounds (Ponomarev et al. 2017; Harrison and Putnis 1999).

Mössbauer spectroscopy

The in-situ Mössbauer spectra of investigated siderites were obtained during heating up to temperature 750 °C and then cooling to room temperature. Figure 3 shows the Mössbauer spectra of the Sd1 siderite sample obtained during heating to 750 °C and subsequent cooling to room temperature and Figs. 4 and 5, and 6 show in-situ Mössbauer spectra of the investigated iron carbonates obtained in selected temperatures during heating and cooling. The obtained hyperfine parameters of all fitting components and their contributions are shown in Fig. 7. Up to temperature 300 °C, all spectra were fitted with a single doublet associated with Fe²⁺ ions in siderite (FeCO₃). The hyperfine parameters, isomer shift (IS_{Sd}) and quadrupole splitting (QS_{Sd}), characterizing this doublet at room temperature (Fig. 7a) are in very good agreement with literature data (Ristić et al. 2017; Shokanov et al. 2020; Zavarzina et al. 2020). In the temperature range of 300–500 °C, the contribution of this component in the Mössbauer spectra decreases to zero (Fig. 7a). In this temperature range, siderite decomposition takes place. Decomposition of siderite leads to the formation of iron oxide nanoparticles (NPS). The component of the Mössbauer spectrum representing these oxides is a ferric quadrupole doublet (Figs. 4 and 5). Up to a temperature of about 450 °C, the concentration of this doublet in the spectrum increases, then with a further increase in temperature, it begins to decrease (Fig. 7d), which can relate to the partial crystallization of the iron oxides represented by it. At temperatures of 700 °C and 750 °C, only the doublet is visible in the spectra (Fig. 6), which will be associated here with the paramagnetic phases of Fe-oxides. Additionally, at a temperature of 350 °C, a sextet with a hyperfine magnetic field of approximately 38 T begins to be visible and temperature 400 °C is the temperature at which magnetic components dominate the spectra (Figs. 4 and 5, and 7b). The two clearly visible sextets have been associated with hematite. Of course, it should be recalled that the Mössbauer spectrum of this iron oxide is represented by one sextet associated with only crystalline lattice site for Fe³⁺ in hexagonal α -Fe₂O₃. However, these sextets may represent different degrees of crystallinity of this iron oxide, and it is also possible that Fe ions are replaced by Al, Mn, or Mg, among others. Both, the size of the crystallites and the impurities in the hematite will cause the magnetic transition to occur in a broader range of temperatures, and in the Mössbauer spectra, we observe this as the appearance of components with smaller fields (De Grave et al. 1999; Berry et al. 2020). Apart from the sextets associated with hematite, its remaining magnetic part is visible in

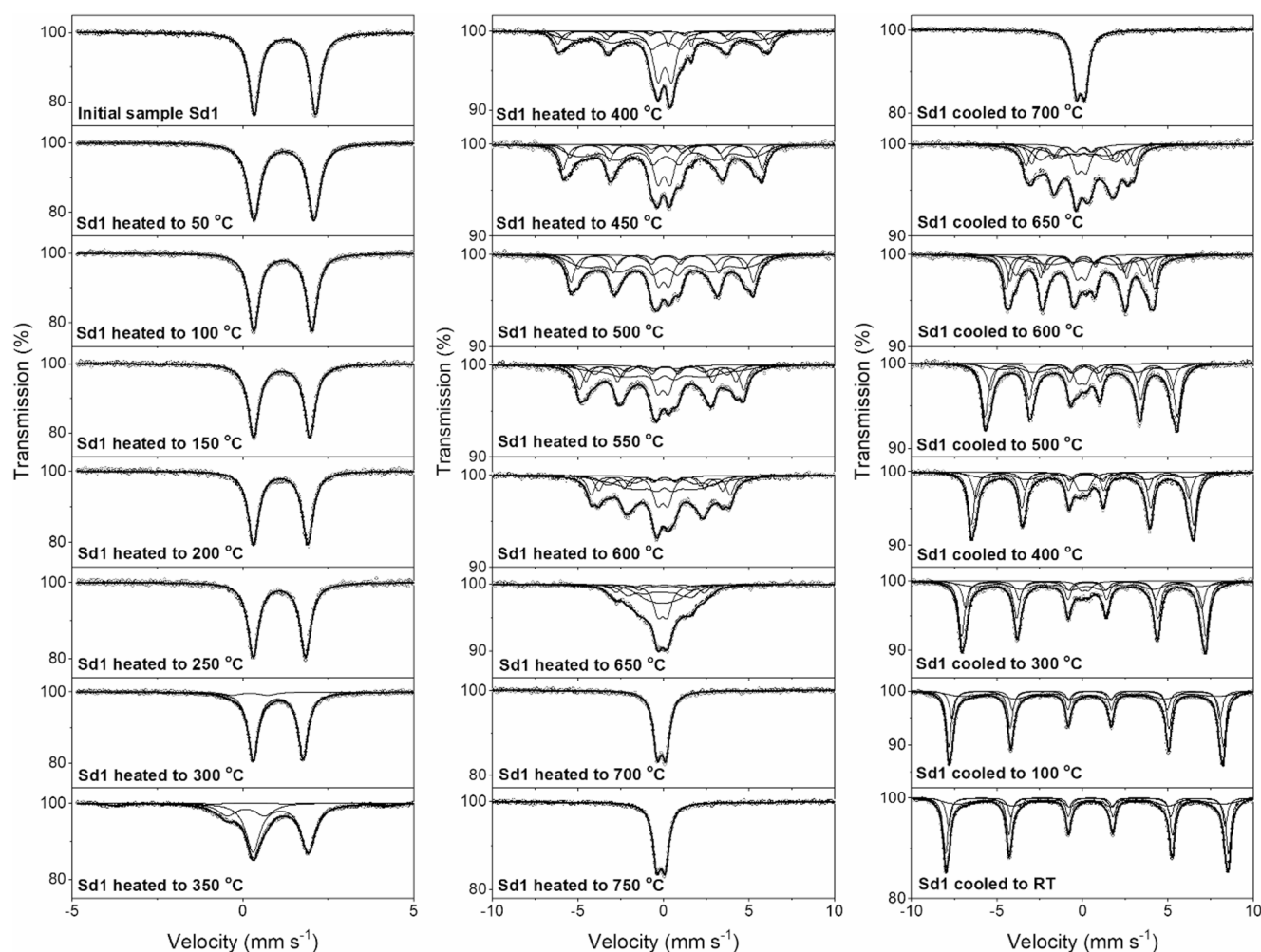


Fig. 3 The in-situ Mössbauer spectra of the Sd1 siderite sample obtained during heating to 750 °C and cooling to room temperature (RT). The experimental points, fitting curves and spectral components are presented

the spectrum but has no clear absorption maxima. X-ray diffraction and magnetic measurements indicate that this part of the spectrum can be related to low crystallinity magnetite. Such magnetite is formed in all heated siderite samples. It is impossible to fit this part of the spectrum with two sextets characterizing Fe ions in the tetrahedral and octahedral coordination in the structure of this spinel. That is why this part of the spectra was fitted with a hyperfine magnetic field distribution. The obtained value of the isomer shift (IS_{Mag}) of this distribution (Fig. 7c) will be the average value characterizing two positions (tetrahedral and octahedral) of Fe ions in magnetite structure, like the value of the hyperfine magnetic field (B_{Mag}) (Fig. 7c). During the cooling process, the contribution of sextets related to hematite is practically constant (Fig. 7b) and the concentration of the magnetic distribution in the spectra is also almost constant up to a temperature of ~400 °C, where a slight increase in the contribution of this component up to room temperature was visible. At the same time, the hyperfine magnetic field B_{Mag}

decreases slightly in this temperature range (Fig. 7c). This effect can be explained by analyzing the hyperfine parameters of the ferric doublet observed in the Mössbauer spectra of the cooled samples (Figs. 4 and 5). The different values of the quadrupole splitting (QS) obtained during the heating and cooling processes (Fig. 7d) suggest that below a temperature of 600 °C, the character of this doublet changes. The values of QS_{NPS} parameter obtained during the heating of the samples are much higher than those calculated during the cooling process. Higher quadrupole splitting values are characteristic of hematite nanoparticles (Bodker and Morup 2000; Bodker et al. 2000). Starting from a temperature of about 400 °C contribution of this doublet begins to decrease with temperature decreasing (Fig. 7d), and below 200 °C is close to zero. This doublet is probably associated with magnesio-magnetite. High Mg content in the magnetite structure significantly reduces the magnetic transition temperature (Ristić et al. 2017), as indicated by the results of magnetic measurements. It is also worth noting that even when the

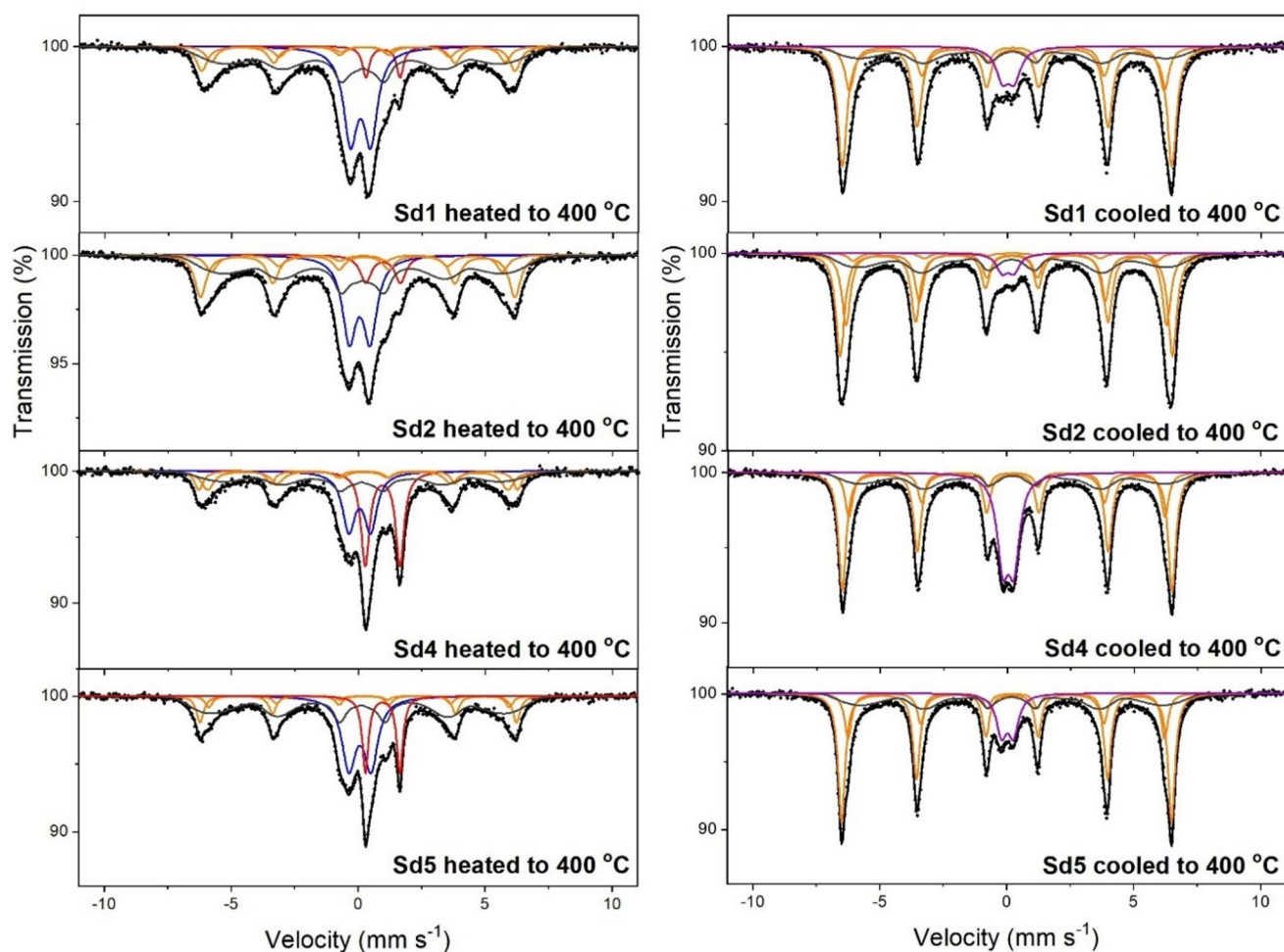


Fig. 4 The in-situ Mössbauer spectra measured for siderite samples heated at 400 °C and after cooled to 400 °C from 750 °C. The experimental points, fitting curves and spectral components corresponding to particular iron sites in different structural and magnetic phases (col-

ored lines) are presented; red line – siderite, orange line – hematite, gray line – magnetite, blue / purple line – iron oxide nanoparticles (hematite or/and magnetite) / magnesio-magnetite

samples are cooled to room temperature, the components related to magnetic distribution have no clear lines related to bulk magnetite. This fact would indicate a high degree of disorder in this phase as well as small sizes of crystal grain. In addition to significant amounts of Mg, samples Sd4 and Sd5 also contained a similar amount of Ca. This element can also be incorporated into the magnetite structure (Jimenez-Lopez et al. 2012), affecting its magnetic and crystalline properties.

Raman spectroscopy

Employing a statistical approach to data collection, Fig. 8 summarizes the three most representative Raman spectra in the 100–1600 cm^{-1} region obtained from distinct areas of siderite decomposition products for selected siderite samples (Sd1 and Sd4). All collected Raman spectra exhibited a

prominent arrangement of hematite ($\alpha\text{-Fe}_2\text{O}_3$) bands in the 200–700 cm^{-1} region, featuring A_{1g} and E_g modes (Fig. 8) correlated with symmetric stretching and bending Fe-O vibrations (De Faria et al. 1997; Chamritski and Burns 2005). Around 1320 cm^{-1} observed a strong band attributed to two-magnon scattering arising from the interaction of two magnons created on antiparallel closed spins. Notably, the positions of the hematite $\alpha\text{-Fe}_2\text{O}_3$ bands varied slightly based on the collection site. Some areas indicated a crystalline bulk hematite phase ($\alpha\text{-Fe}_2\text{O}_3^b$) (De Faria et al. 1997; Chamritski and Burns 2005), while others suggested an Al-doped or more nanocrystalline form of hematite ($\alpha\text{-Fe}_2\text{O}_3^n$) (Srivastava et al. 2010). Interpretative challenges in Raman spectra of investigated samples arose concerning an additional band observed in the 650–670 cm^{-1} range. Multiple hypotheses exist for the origin of this band, including surface resonance of incomplete symmetry of hematite,

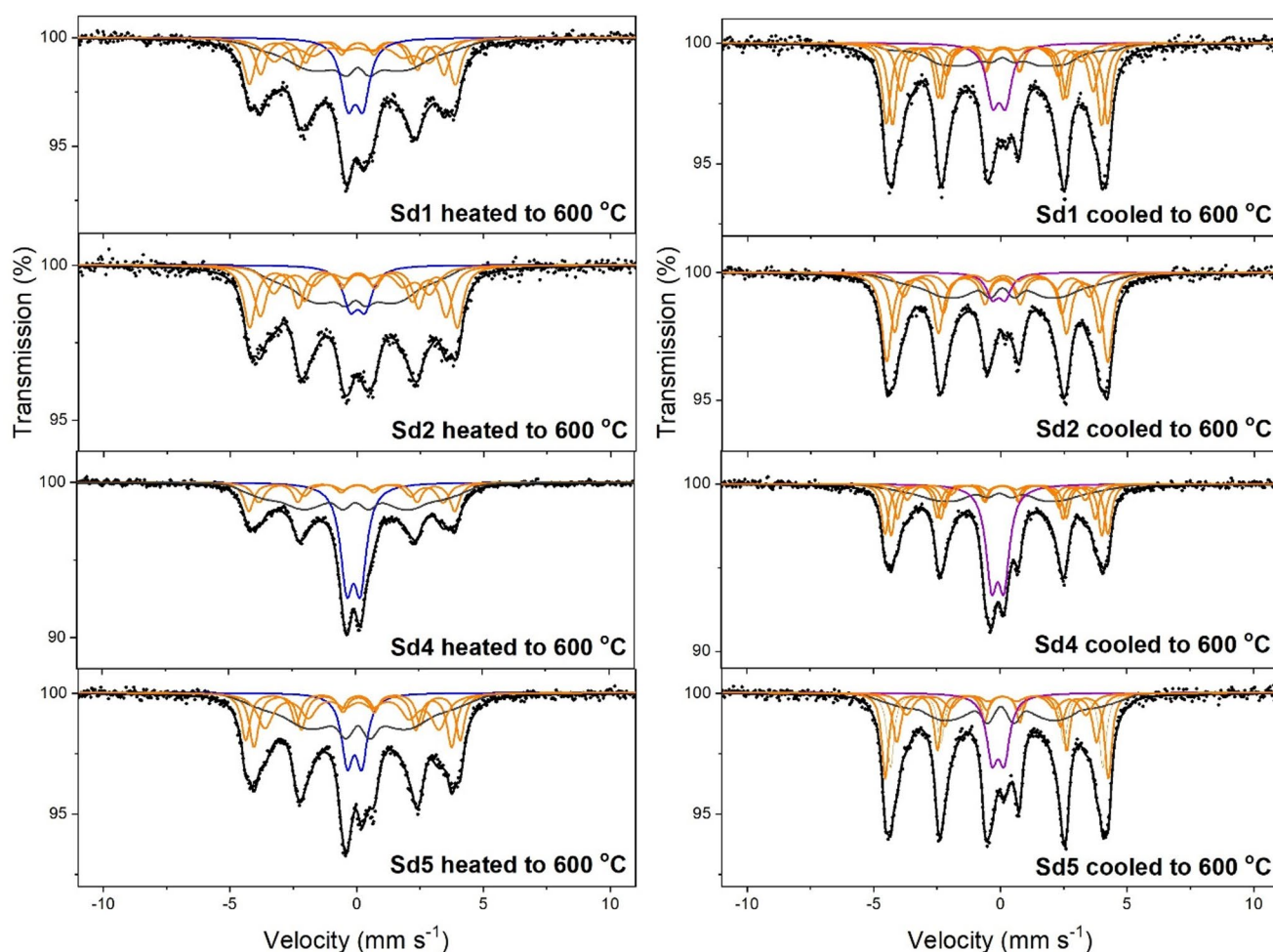


Fig. 5 The in-situ Mössbauer spectra measured for siderite samples heated at 600 °C and after cooled to 600 °C from 750 °C. The experimental points, fitting curves and spectral components corresponding to particular iron sites in different structural and magnetic phases (col-

ored lines) are presented; orange line – hematite, gray line – magnetite, blue / purple line – iron oxide nanoparticles (hematite or/and magnetite) / magnesio-magnetite

stress-induced defects, the first overtone of the two-magnon scattering band (Shim and Duffy 2001), and contamination or impurities (Gasparov et al. 2000; Zoppi et al. 2005). Some papers reported that this band is also related to the A_{1g} mode in orthorhombic magnetite structure (Verble 1974; Gasparov et al. 2000). As a result, on one side the bands observed on the Raman spectra suggested surface resonance or stress-induced defects in hematite, while in others, their nature was related to the coexistence of hematite with magnetite (grey-colored band in Fig. 8). The latter hypothesis suggests that the A_{1g} -magnetite band position around 663–664 cm^{-1} is related to a less defective phase, while its shift toward lower frequencies points to a more defective spinel structure. These findings underscore the complex interplay of factors influencing Raman spectra and microscopic phase heterogeneity with different degrees of structure order depending on the locations.

Transmission electron microscopy

The structure and morphology of the Sd1 and Sd4 samples, obtained after heating to 750 °C and cooling to room temperature, were analyzed using scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The recorded STEM and TEM images (Figs. 9 and 10) highlighted the irregular shapes of the investigated materials for both Sd1 and Sd4. In addition, high-resolution TEM images (Fig. 9c and d, and 10d) showed their crystalline nature with clearly visible crystalline planes. For sample Sd1, the presence of crystals with interplanar distances of (~ 0.36 nm) and (~ 0.285 nm) which can be identified as (012) planes of the rhombohedral hematite and (022) planes of face-centered cubic (fcc) magnetite, respectively, was observed (Fig. 9d). On the other hand, for

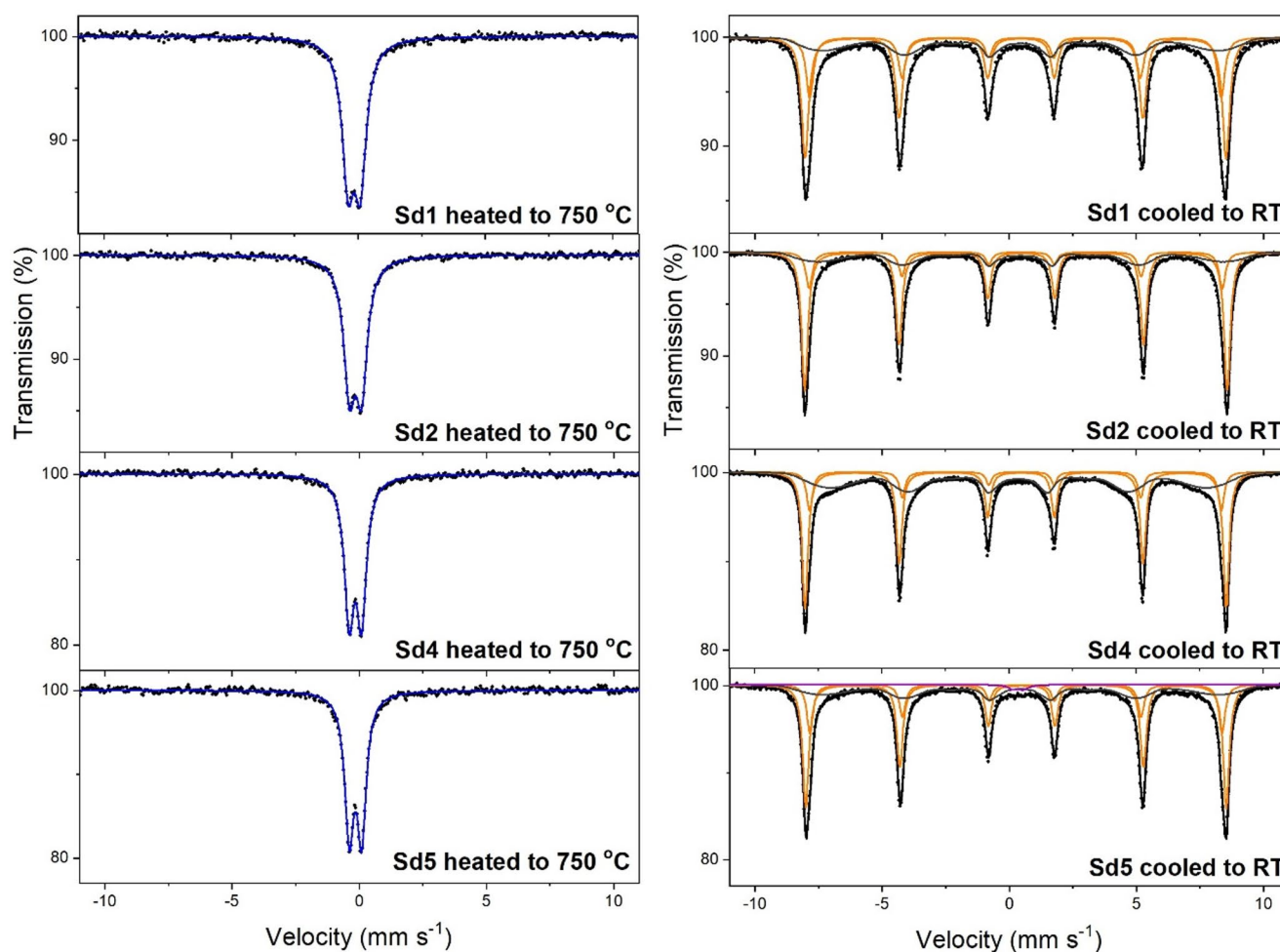


Fig. 6 The in-situ Mössbauer spectra measured for siderite samples heated at 750 °C and after cooling them to room temperature (RT). The experimental points, fitting curves and spectral components cor-

responding to particular iron sites in different structural and magnetic phases (colored lines) are presented; orange line – hematite, gray line – magnetite, blue line – iron oxide nanoparticles

sample Sd4, crystals with lattice distance (~ 0.26 nm) were recorded which, in turn, can be attributed to (110) planes of the rhombohedral hematite.

Discussion

X-ray diffraction and ^{57}Fe Mössbauer measurements of all studied carbonate rocks showed that the only iron-containing mineral present was siderite (FeCO_3). The highest content of this mineral (Table 2), approximately 94%, was found in the Sd1 sample, whereas the lowest content occurred in the Sd5 sample ($\sim 79\%$). Other minerals present in the samples are mainly dolomite ($\text{CaMg}(\text{CO}_3)_2$) and quartz (SiO_2), which account for the elevated contents of Mg, Ca, and Si, particularly in the Sd4 and Sd5 samples. The bulk chemical composition determined by XRF, combined with XRD results, confirms that iron is hosted exclusively in siderite before heating. In contrast,

non-iron oxides originate from accessory silicate and carbonate phases. This compositional framework provides a reliable reference for interpreting the phase transformations observed during subsequent thermal treatment. The fact that iron is located only in siderite allows the use of ^{57}Fe Mössbauer spectroscopy to investigate the transformations that this mineral undergoes at high temperatures under vacuum conditions.

The crystal sizes obtained by X-ray diffraction (XRD) are confirm that the iron oxides formed by siderite decomposition, especially magnetite, are poorly crystalline, with average crystallite sizes of 10–30 nm.

The magnetic and the in-situ ^{57}Fe Mössbauer measurements (Figs. 2, 3, 4, 5, 6 and 7) show that in temperature range from 300 °C to about 500 °C the siderite decomposition process take place. We assume that in this temperature range and under vacuum atmosphere ($\sim 2 \cdot 10^{-5}$ Pa) siderite transformation into magnetite according to equation (Lietzke and Mullins 1981; Mendoza et al. 2019):

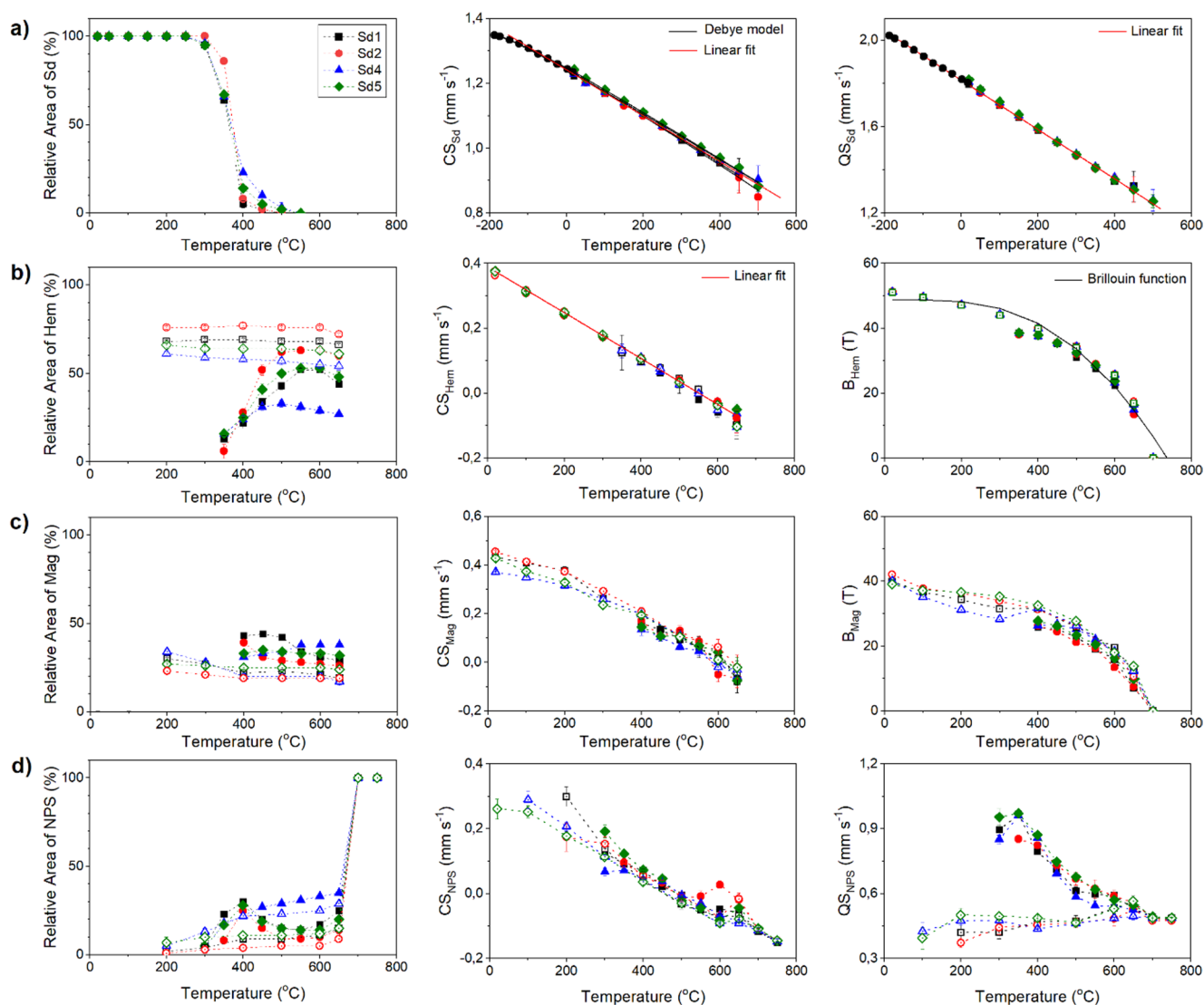
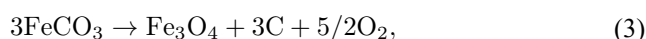
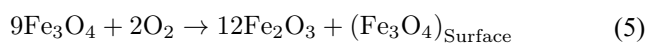
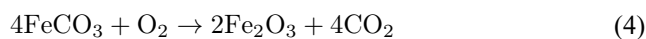


Fig. 7 Relative area of components in Mössbauer spectra and their hyperfine parameters versus temperature for siderite Sd **a**), hematite Hem **b**), magnetite Mag **c**), and iron oxides nanoparticles NPS (hematite or/and magnetite) **d**). The full colored points characterize the parameters during heating, and the hollow points describe the param-

eters during the cooling of the sample. The dashed lines indicate the trends of the data and act as a guide to the eye. The black dots in the CS(T) and QS(T) plots for siderite are from (De Grave and Van Alboom 1991). The isomer shifts are given relative to α -Fe at room temperature



The above reaction also allows for the formation of hematite, but two paths are possible, illustrated by the equations below (McCarty et al. 2014; Mendoza et al. 2019):



Based on Eqs. (3) and (4), we can conclude that hematite is formed only when siderite is present in the sample. Additionally, here Eq. (5) requires a brief comment. At higher

temperatures, oxidizing Fe^{2+} ions to Fe^{3+} ions in magnetite leads to hematite, but magnetite and hematite have different crystal symmetries; for this reason, hematite domains must nucleate before they can grow (Lyubutin et al. 2009; McCarty et al. 2014). As was shown (McCarty et al. 2014), the high-temperature oxidation grows magnetite at the surface and hematite in the interior. It means that different reactions occur in the interior (where hematite forms) and at the surface (where new magnetite forms) (McCarty et al. 2014). Moreover, in addition to the common symmetry of calcite and hematite, these minerals share an analogous arrangement of oxygen atoms. The O atoms in siderite and hematite are (distorted) hexagonally close-packed, whereas in

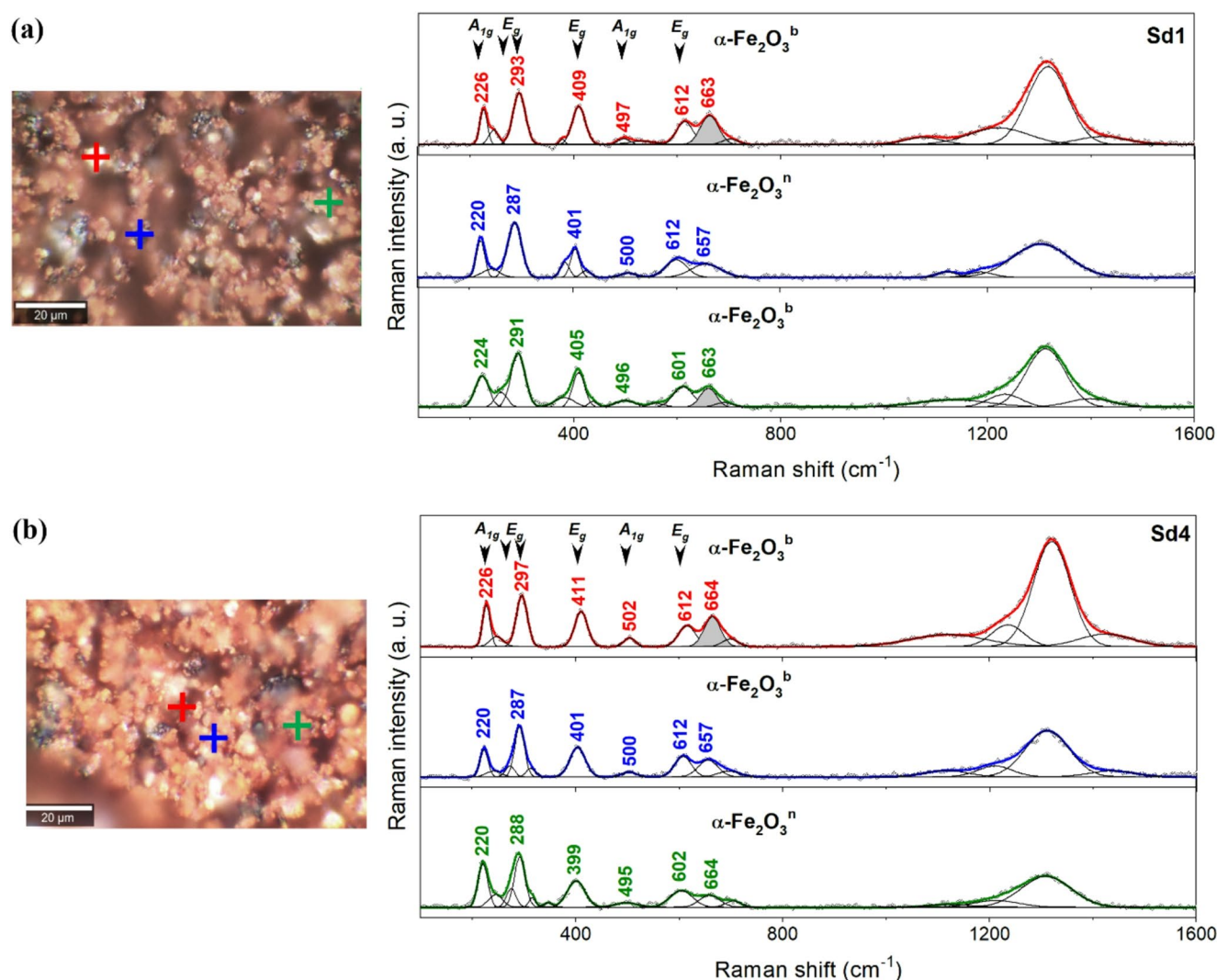


Fig. 8 Raman spectra of heat-treated siderite Sd1 (a) and Sd4 (b) up to 750 °C and cooled down to RT. Spectra were gathered from a few points (red, blue, and green), while color crosses corresponded

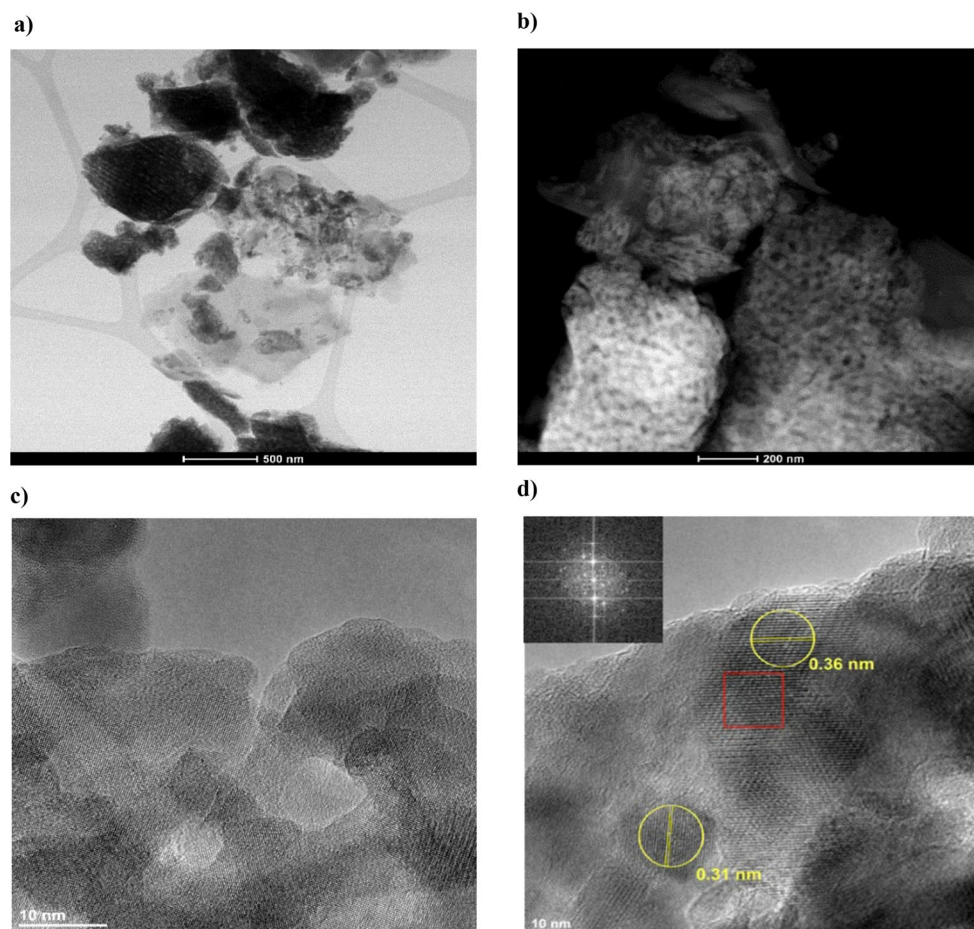
to the individual spectra. Grey-colored bands corresponded to Fe_3O_4 , while other bands originated from hematite $\alpha\text{-Fe}_2\text{O}_3$ (a nanocrystalline ($\alpha\text{-Fe}_2\text{O}_3^n$) or an Al-doped and crystalline bulk phase ($\alpha\text{-Fe}_2\text{O}_3^b$))

magnetite they are cubically close-packed. Therefore, maintaining this approximate arrangement of O atoms allows for easy migration of cations. As shown in Eq. (5), for every 12 formula units of $\alpha\text{-Fe}_2\text{O}_3$ created one unit of Fe_3O_4 is added to the surface. The hematite and magnetite thus formed will have different degrees of crystallization. The abovementioned processes occur in a narrow temperature range, up to 500 °C. This is the temperature at which siderite completely decomposes. It should be noted that hematite is formed in portions from magnetite and in the process of siderite decomposition. This also explains the presence of more than one component in the Mössbauer spectra related to this iron oxide, differing slightly in hyperfine parameters, particularly in the hyperfine magnetic field. It should be remembered that hematite is formed as a final effect of siderite decomposition in air (Pan et al. 1999, 2000; Kądziołka-Gaweł et al.

2025), and magnetite is the main product of this process in a vacuum (Wang et al. 2015; Zhu et al. 2016). The presence of hematite in the studied processes may indicate that they occur very rapidly, i.e., faster than the gas removal process from the sample chamber. However, it is certain that hematite is formed as a result of oxygen generation in the reaction described by Eq. (3) and is formed only until the siderite is completely decomposed.

The temperature dependence of hyperfine parameters characterizing the ferrous doublet associated with siderite was calculated. The temperature dependence of CS(T) is described by Eq. (1). However, to determine from Eq. (2) the value of the Debye temperature Θ_D , low-temperature measurements are necessary because at high temperatures this dependence can be approximated by a decreasing linear function (Bhide and Hegde 1972; Podgórna et al. 2017).

Fig. 9 Structure and morphology of Sd1: **a)** BF-STEM and **b)** HAADF-STEM images; **(c, d)** HRTEM images of Sd1 with measured lattice spacing (the inset image shows the received fast Fourier transform from enlarged red marked area on d)



For this reason, the low-temperature $CS_{Sd}(T)$ dependency for siderite presented by De Grave and Van Alboom (1991) were used to determine the temperature Θ_D . The experimental data and the fitted curves are presented in Fig. 7a. It is worth noting that the obtained $CS_{Sd}(T)$ values for siderite in the low temperature range (De Grave and Van Alboom 1991) are well correlated with those obtained in this work. The obtained Debye temperature values for siderite in individual samples are: 424(35) K, 324(37) K, 454(54) K, and 379(27) K for samples Sd1, Sd2, Sd4, and Sd5, respectively. The determined temperatures differ slightly from those presented in the literature, which are 345 K (De Grave and Van Alboom 1991) and 375 K (Ellwood et al. 1989). One of the reasons for such differences, also in literature values, may be the fact that for a given absorber, the value of Θ_D will generally be different from that estimated by the surface method (De Grave and Van Alboom 1991) or using the SOD equation (Ellwood et al. 1989). As we know, such parameters as lake center shift or recoilless fraction give different information on the lattice dynamics, i.e., the former on the mean square velocity and the latter on the mean-square displacement, the vibrating atoms. Consequently, Θ_D values are usually different, as determined from these two approximations.

Therefore, 375 K (Ellwood et al. 1989) should be the reference temperature here. The temperature Θ_D obtained for the Sd5 sample is closest to it, and the differences observed in the other samples may result from defects or impurities in the siderite structure that affect lattice dynamics.

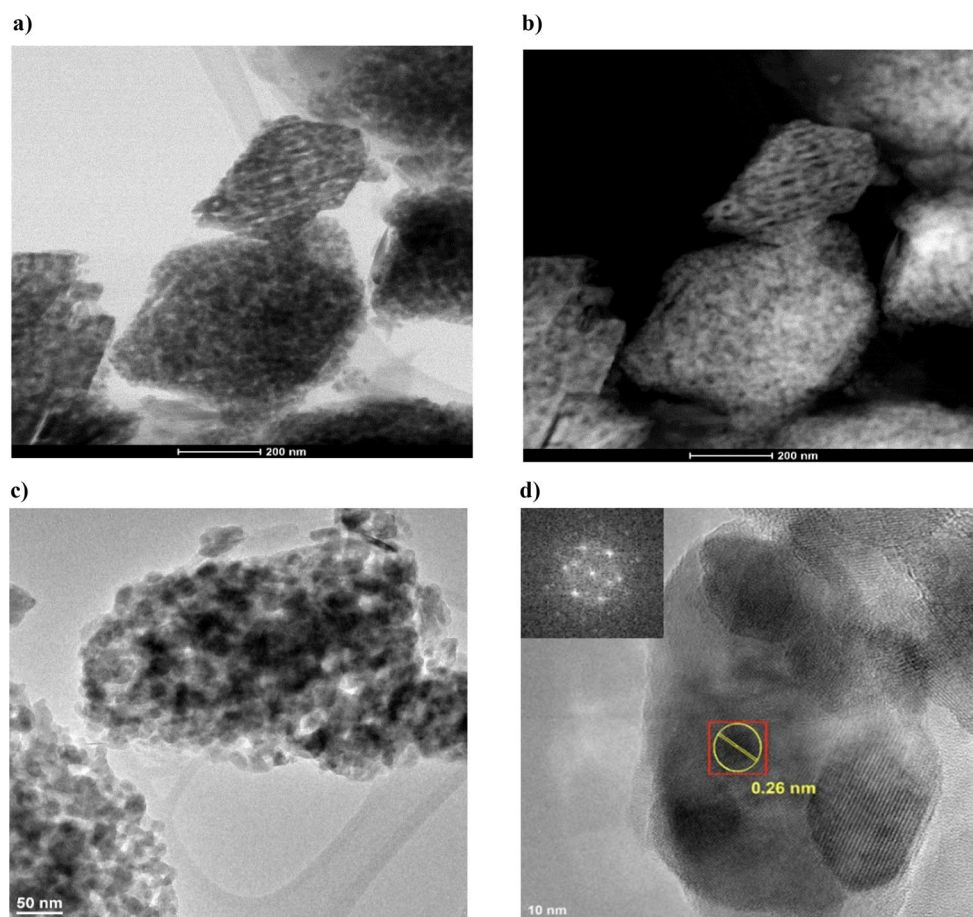
Omitting the low temperature range where the center shift versus temperature is not linear, a linear $CS_{Sd}(T)$ dependence was fitted for siderite over a wide temperature range (–200–500 °C). Linear temperature dependence was also determined for the quadrupole splitting $QS_{Sd}(T)$ (Fig. 7a) additionally using data from (De Grave and Van Alboom 1991). These temperature dependencies are presented in Eqs. (6) and (7) below:

$$CS_{Sd}(T) = -0.00071(1)T + 1.242(3) \quad (6)$$

$$QS_{Sd}(T) = -0.00113(1)T + 1.814(2) \quad (7)$$

Based on Eqs. (6) and (7), it is easy to determine the values of IS_{Sd} and QS_{Sd} for siderite in a wide temperature range, in particular at room temperature (20 °C), they will be equal to 1.223 mm s^{–1} and 1.791 mm s^{–1}, respectively. Additionally, special attention should be paid to the observed strongly linear dependence of the Fe²⁺ quadrupole splitting on temperature,

Fig. 10 Structure and morphology of Sd4: **a)** BF-STEM and **b)** HAADF-STEM images; **c)** TEM and **d)** HRTEM images of Sd4 with measured lattice spacing (the inset image shows the received fast Fourier transform from enlarged red marked area on d)



which is not expected from ordering the electron eigenstates in a static carbonate crystal (Srivastava 1983). It is assumed that vibronic coupling (or orbit-lattice interaction) plays an important role in generating the observed “anomalous” temperature dependence of the quadrupole splitting in FeCO_3 and similar compounds (Price 1978; Srivastava 1983; De Grave et al. 1982; De Grave and Vochten 1985).

The magnetic and the in-situ ^{57}Fe Mössbauer measurements also show that the observed changes occurring during heating the samples at temperatures higher than 500 °C are related to magnetic transitions in the formed iron oxides (magnetite and hematite). Figure 6b shows the change of average isomer shift IS_{Hem} and hyperfine magnetic field B_{Hem} versus the temperature of all magnetic components representing hematite during the heating and cooling of all siderite samples. The average value means a weighted average for all components representing $\alpha\text{-Fe}_2\text{O}_3$. Equation (8) shows the dependence of the center shift versus temperature for hematite in the temperature range of 20 °C ÷ 650 °C:

$$\text{CS}_{\text{Hem}}(T) = -0.00071(1) T + 0.388(2) \quad (8)$$

The isomer shift value determined from Eq. (8) at room temperature (20 °C) is 0.374 mm s^{-1} . This is a typical value

for this iron oxide at room temperature (Bodker and Morup 2000; Bodker et al. 2000; Masina et al. 2024), thus confirming the correctness of the interpretation and way of fitting of the Mössbauer spectra. Similarly to the values of the hyperfine magnetic field (B_{Hem}) in RT, which are slightly above 51 T. The dependence of B_{Hem} on temperature was fitted with the Brillouin function (Fig. 7b) and is consistent with the literature data (Lyubutin et al. 2009; McCarty et al. 2014; Berry et al. 2020).

Magnetite (Fe_3O_4) is an oxide belonging to the group of iron spinels, which is formed during siderite decomposition and a small amount of it is generated during the formation of hematite, attracts particular attention. X-ray, Raman, TEM, and Mössbauer measurements show that this iron oxide formed in the abovementioned processes is slightly crystalline during heating and remains in such form even after the sample is cooled to room temperature. In samples (Sd4 and Sd5) containing more significant amounts of Mg (Table 1), we also observe the incorporation of this element into the structure of magnetite and the formation of the so-called magnesio-magnetite.

The ferric doublet also appears in Mössbauer spectra and, as noted above, it relates to the nanocrystalline or paramagnetic form of iron oxides. Due to the type of crystal structure of iron

oxides, such components differ in their quadrupole splitting values, but the isomeric shift values are similar to them (Fig. 7d).

Conclusions

The presented study shows the results of the thermal decomposition mechanism of siderite in vacuum ($2 \cdot 10^{-5}$ Pa). The phase analysis of iron-bearing minerals formed during these processes is shown. Most of the conclusions were drawn based on the results of in-situ Mössbauer measurements. This technique is an excellent tool for identifying iron-containing minerals and tracking the processes they undergo, such as temperature. Importantly, we get a macroscopic image of the whole sample and the local information that composes it because, as we know, we use the Fe nucleus as a probe of the local environment in this technique. The results of the measurements show that the siderite decomposition process takes place in the temperature range of 300–500 °C. The main product of this process is magnetite, and hematite is also formed during its oxidation. Importantly, hematite can form if siderite is present in the sample. Based on the results of Mössbauer measurements, temperature dependences of hyperfine parameters were obtained for siderite or hematite in a wide temperature range, which will make it easier for future Mössbauer researchers to analyze the high temperature spectra of these minerals or materials containing them.

It should be noted that the applied vacuum ($2 \cdot 10^{-5}$ Pa) may not be sufficient to remove all residual gases (e.g., O_2 or H_2O). Under these conditions, partial oxidation of Fe^{2+} ions to Fe^{3+} ions in magnetite leads to hematite formation, which may partly explain its presence. However, the studies conducted do not show the typical reactions observed for siderite decomposition in high vacuum or an air atmosphere. This suggests that the process of siderite decomposition strongly depends on external conditions and may proceed differently even with small changes in them and may also be influenced by factors such as heating time.

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Author contributions M.K.-G. did the conceptualization; designed the methodology; and performed the measurements/investigations, and validation. She also prepared the original draft and reviewed and edited the manuscript, secured the resources; investigation, M.K.-G., M.D., P.G., D.Ł., and M.W.; formal analysis, M.K.-G., Z.A., M.D., D.Ł., and J.G. All authors agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

Data availability The data may be made available by the authors upon individual request.

Declarations

Competing interests The authors declare no competing interests.

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