



^{57}Fe Mössbauer Spectrometry to explore natural and artificial nanostructures

Virender K. Sharma^{1,a)}, Zoltan Homonnay², Tetsuaki Nishida³, Jean-Marc Greneche⁴

¹ Program of Environmental and Sustainability, Département of Environmental and Occupational Health, School of Public Health, Texas A&M University, Texas, USA

² Laboratory of Nuclear Chemistry, Eötvös Loránd University, Budapest, Hungary

³ Environmental Materials Institute, Fukuoka, Japan

⁴ Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, IMMM, Le Mans Université, Le Mans, France

^{a)} Address all correspondence to this author. e-mail: vsharma@tamu.edu

Virender K. Sharma, Zoltan Homonnay, Tetsuaki Nishida, and Jean-Marc Greneche were guest editors of this journal during the review and decision stage. For the JMR policy on review and publication of manuscripts authored by editors, please refer to <http://www.mrs.org/editor-manuscripts/>.

Received: 18 January 2023; accepted: 3 February 2023; published online: 10 March 2023

Since its discovery in the middle of the twentieth century, ^{57}Fe Mössbauer spectrometry has been increasingly applied to a variety of scientific topics, including fundamental and industrial ones, going from basic chemistry, materials science, earth sciences to biology and archeology. Indeed, its high atomic scale sensitivity to local order combined with easy and low cost facilities have convinced scientists to use this tool as a nice complement to other techniques. This article serves as an introduction to this special issue dedicated to the application of Mössbauer spectrometry to the study of both laboratory-made and natural materials, each with relevant specific properties: it shows that the significant contribution of this local probe technique is underlined for each type of material, allowing a better understanding of the synthesis mechanisms, the chemical and/or physical properties.

Mössbauer Spectroscopy dates back to the fifties of the twentieth century when Rudolf Mössbauer discovered the effect later named after him: expectedly a curiosity in physics that may not have a great number of applications. Yet the strongest driving force to develop a branch of spectroscopy based on the recoilless gamma emission/absorption was the extremely high energy resolution it offered. Nevertheless, since the gamma photon carries information on energy states within the nucleus, it was not clear *a priori* whether this spectroscopy would be suitable to observe chemical changes, i.e., energy shifts assigned to structural changes in the valence shell of atoms (either in a molecule or in a crystal lattice). Later one could witness the lucky situation that although these 1–10 mV chemical energy shifts are substantially damped while reaching the nucleus, the 10^{-9} eV energy resolution there (for ^{57}Fe) is enough to observe these changes. On top of that, the most suitable nuclide for Mössbauer Spectroscopy is ^{57}Fe , an isotope of iron that is one of the most important elements on Earth.

Thus ^{57}Fe Mössbauer Spectrometry became a very unique tool for researchers from solid state physics to chemistry to even biology in systems where iron plays a role. The Mössbauer nuclide provides information on its nearest environment on the atomic scale, so this is a local method, and, as such, it is especially sensitive to surface effects. This gives ground to its applications in the study of nanostructures created by nature or man. An example of using Mössbauer Spectrometry to characterize local structures of pure and doped iron oxides and hydroxides nanoparticles is reviewed in this issue. Iron oxides nanoparticles (IONPs) are widely used in various applications such as magnetic storage media, biomedicine, metalloenzymes, electrocatalyst, and water remediation and thus make Mössbauer Spectrometry an attractive tool to gain information on magnetic and electric field at the probe nuclei due to spin and charge in the valence shell of the Mössbauer active atoms like iron [1, 2]. Below are examples in natural and artificial microstructures and nanostructures that are presented in this special issue.

Natural systems

Nanostructures in nature can form for various reasons. The crystal structure of the given compound may have heterogeneities on the atomic scale. A classic example is the case of zeolites with their intrinsic property that there are voids/cages of various sizes in the silicate framework that makes them applicable in technologies where adsorption or catalysis is in focus. For Mössbauer Spectrometry, iron containing zeolites are important and such systems have been investigated in the past decades extensively [3, 4].

There is an increasing knowledge on sedimentary iron ores that the formation of these ores is of biologically mediated in many cases, i.e., the small particles of ferrihydrite, goethite, hematite, etc. are products of microbial activity and that is the reason of the micro/nano scale particle size [5]. This creates quite a challenge in Mössbauer Spectrometry because magnetic relaxation effects distort the otherwise regular line shape in the spectra. These distortions are partially due to the particle size (superparamagnetic relaxation) and natural impurities (shift in the magnetic transition temperature). Figure 1 shows an example on paleo soils containing goethite and hematite as iron bearing minerals. The top spectra show that at room temperature, the goethite and hematite are indistinguishable while at 80 K each is represented by its own sextet (with some remanent superparamagnetic goethite at 80 K, indicated by the central doublet). The

bottom spectra demonstrate another case when mostly impurities cause magnetic hyperfine field distribution (not shown) for both hematite and goethite at room temperature while at 80 K two (although badly overlapped) sextets can be evaluated.

In certain cases a natural system may be a precursor for the production of nano systems that can be used for some industrial purpose. Kaolin is a layered silicate with an empirical formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (1:1 type dioctahedral phyllosilicates). The double tetrahedral Si-O plus octahedral Al-O layers can be separated/delaminated by intercalation/exfoliation technique and the new structure is composed of nano scrolls (the separated double layers roll up) with extremely high specific surface area. This technique is, however, hindered by the iron content of the natural kaolin: goethite, hematite as separate phases as well as structural iron substituting for aluminum at the octahedral sites [6]. Controlling the chemical form of iron during the technological process is of primary importance, shown in more details in this Focus Issue.

Naturally occurring nanoparticles of iron oxides and oxyhydroxides are important in soils where their chemical interaction with the organic soil constituents is decisive in the iron uptake by plants [7].

In meteorites, nanostructured and/or amorphous phases are frequently observed possibly due to the formation history of the meteorite and the heating and fast cooling when it falls to the Earth surface [8].

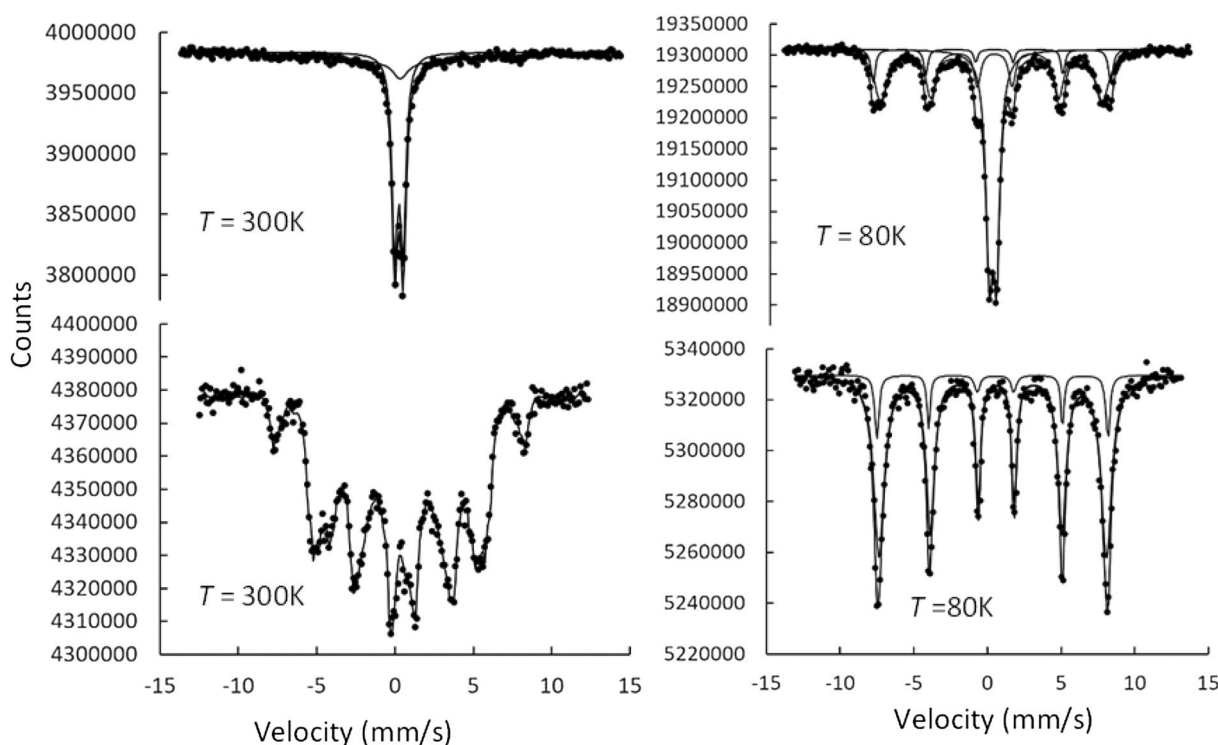


Figure 1: Mössbauer spectra of two paleo soil samples containing goethite and hematite. The astonishing difference between the 300 K and 80 K spectra is due to superparamagnetism (top) and lattice impurities (bottom).

Mössbauer spectrometry is an important tool in studying the redox processes to understand the biogeochemical cycling of iron and the degradation of organic compounds in the solid–liquid interface of the environment [9, 10]. Comprehending the redox processes may shed light on the mobility and toxicity, and the persistence of organic pollutants present on the surface of environments. In other words, transformation of Fe^{II} to Fe^{III} or vice versa may drive the transformation of organic pollutants, which is shown in Figure 2.

In the study presented in this special issue, the authors applied Mössbauer spectrometry to determine Fe^{II} and Fe^{III} contents in geochemical transformations to obtain the rates and mechanisms of important reactions in the environment. The study showed that oxidants such as O_2 and the reducing Fe^{II} assist in electron transfer, precipitation, and dissolution reactions of geochemical importance.

Artificial systems

Iron is often applied in various catalysts in the form of mixed oxides. Especially good partners are: Cr, Mn, Mo, Re. However, the simple and inexpensive synthesis of such mixed oxides is not straightforward. A physical mixture of the separately synthesized metal oxides needs high temperature and long synthesis because the solid–solid reaction requires mutual diffusion of the metal components. The sol–gel method is a major step to reduce the time and temperature requirement because the co-precipitation from solution with the help of an organic (therefore later removable) framework

provides nanoscale mixture of the metal components right at the beginning of the heat treatment. The ultimate molecular level perfect mixing can be achieved if the two metal components are present in the same compound. For example, if in a salt the cation is Fe^{III} or its organic complex form, and the anion is dichromate, the final mixture is a mixed Fe–Cr-oxide that forms at the lowest possible temperature (compared to the direct and sol–gel method). Applying mixed anions, e.g., dichromate plus nitrate, since the latter is automatically removed during the heat treatment, the Fe to Cr ratio can be set in a certain range.

Since iron(III) is not willing to form salts easily with anions like permanganate or dichromate, a good selection for a complex cation is the hexaurea-iron(III) salt. These complex salts can readily form as precipitates or crystals from an aqueous solution. However, the Mössbauer characterization of the starting hexaurea-iron(III) salts is challenging due to the strong relaxational broadening of the Mössbauer spectra [11–18]. The large size of the cation, due to the six urea ligands, results in a large Fe–Fe distance in the lattice, causing a decrease in the paramagnetic spin relaxation and thus a distortion of the lorentzian line shape.

The Mössbauer analysis of the resulting oxides is simpler as it allows observation of mainly bulk properties, but in the case of the final mixed oxide, bixbyite, which was produced from iron hexaurea permanganate, only the Mössbauer spectra could reveal that two types of bixbyite were formed with the same stoichiometry but different crystallographic structure, as was verified later by X-ray diffraction (XRD) [19].

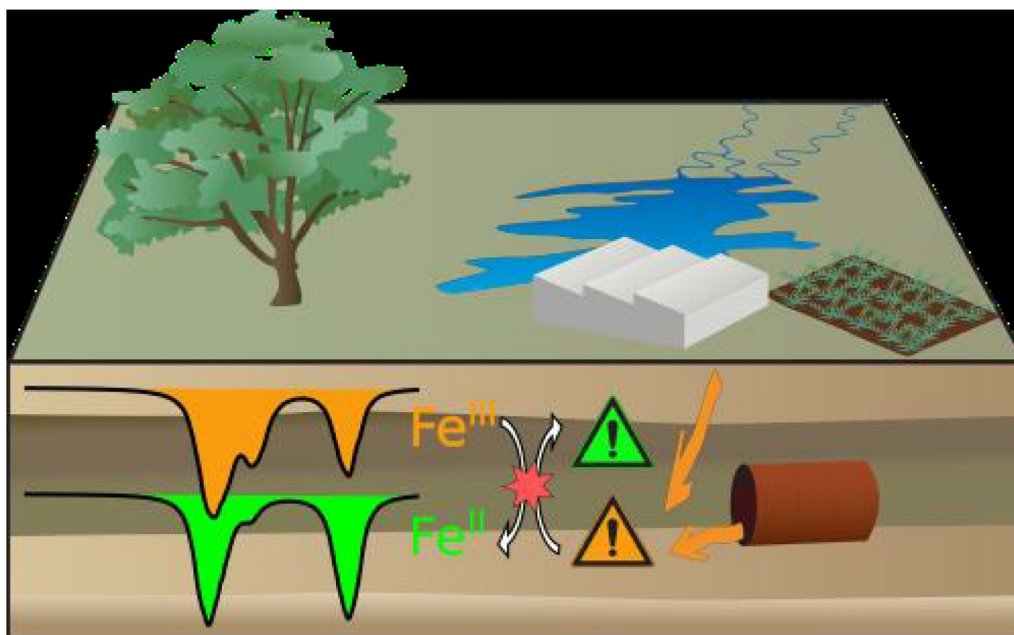


Figure 2: Redox reactions of iron influencing the environment.

Peroxydisulfate is also a good choice as starting anion in $[\text{Fe}(\text{urea})_6]_2(\text{S}_2\text{O}_8)_3$ because it can be removed from the system during the thermal treatments, transforming the compound into FeSO_4 and eventually into $\alpha\text{-Fe}_2\text{O}_3$, as presented in this Focus Issue.

Iron oxides and oxyhydroxides are highly versatile compounds although not only because of the different crystal structures and stoichiometries [20] but impurities, and even more interestingly, the particle size and shape lead special characteristics to the prepared material. Magnetite is particularly important because of its ferrimagnetism that offers sophisticated applications as thermomagnetic treatments in medical practice, where the nanoscale of the particles is of critical importance. Nanoparticles of magnetite can be shaped from a spherical to fibrous outfits by different synthesis routes [21–24]. Mössbauer Spectrometry has been extensively applied to study these systems [25, 26], and magnetite is of particular interest due to the fast electron hopping process between the octahedral iron sites of the inverse spinel type lattice resulting in a +2.5 oxidation state for iron above the Verwey temperature [27, 28]. In the typical Mössbauer spectrum of a stoichiometric, perfectly crystallized magnetite, there are two magnetic sextets with an area ratio 1:2: the respective values of isomer shift allow the former to be assigned to tetrahedral iron sites and the latter to octahedral ones. This is readily explained by the ratio of the corresponding lattice sites in the unit cell. However, it is very frequently observed that the magnetic sextet assigned to the tetrahedral sites has an abnormally high intensity (sometimes the ratio is reciprocal, 2:1) [28–31], and this is mainly due to the lack of stoichiometry of the magnetite and/or the nanometric size of the particles. In the latter situation, the surface area of the magnetite nanoparticles always has a strongly defective stoichiometry and can be partially oxidized to maghemite, the Mössbauer spectrum of which strongly overlaps with the „tetrahedral sextet” of magnetite. With high-quality zero-field Mössbauer spectra, the thickness of the superficial shell and thus the diameter of the core region of magnetite nanoparticles can be estimated assuming a core–shell model which consists of ideal stoichiometric magnetite and maghemite, respectively [26, 28, 32–34]. In addition, low temperature Mössbauer spectra under external magnetic field can be used to estimate the shell thickness of a disordered magnetic structure and the diameter of the collinear ferrimagnetic core or magnetite as well as ferrite nanoparticles, assuming a core–shell magnetic model [26, 35].

Being aware of the importance of the kinetics and mechanism of precipitation when these oxides are prepared from aqueous solutions, forced hydrolysis, is a good tool to influence the morphology of the final product (Figure 3, [36]). The presence of a second cation or some organic material as a potential transient complexing agent can determine the final size and shape of the

ferrhydrite, goethite, hematite and even akaganeite particles, as discussed also in this Focus Issue.

An interesting electromagnetic property of hematite is the Morin transition which is a magnetic phase transition where the antiferromagnetic ordering changes direction with respect to the Electric Field Gradient, namely, it is aligned perpendicular to the c-axis of the lattice above the Morin temperature (T_M) and it is parallel to the c-axis below T_M . Hematite is found paramagnetic above the Curie temperature (T_C), it becomes weakly ferromagnetic (due to spin canting in the antiferromagnetic system) when crossing T_C down to the Morin temperature where there is a transition to unperturbed antiferromagnetism. For pure and well-crystallized hematite, the T_C and T_M are about 955 K and 264 K, respectively, as reported by Stucki et al. [38]. The quadrupole splitting/shift is characteristic for each magnetic type: +0.43 mm/s [39] for paramagnetic hematite, around -0.20 mm/s for weakly ferromagnetic hematite, and +0.41 mm/s for antiferromagnetic hematite [40]. But these values have to be also correlated to the crystallinity of hematite [37].

One has already seen in natural samples that, usually due to Al impurity (in aluminosilicate host rock formations), the Morin temperature of hematite is shifted mainly below 80 K [41]. Thus the change in the Morin transition (increase or decrease) can be an indication of whether in an experiment where an impurity is supposed to be embedded in the host lattice it really took place or did not. Pt and Ru doping of electrospun hematite fiber and its influence on magnetic, photocatalytic and optical properties are also reported in this Focus Issue.

The amorphous state of matter may be considered as the next step in going to even lower spatial dimensions in describing material structure, but it is not necessarily connected directly to the morphology and particle size. Amorphous state in the practical sense means „X-ray amorphous” when diffraction peaks cannot be observed due to the too small regions of unperturbed periodicity in a crystal lattice. This, of course, can be due to very small nanoparticles, but lattice perturbations are on the nanoscale, anyway in amorphous state.

Mössbauer Spectrometry can be especially helpful in material characterization when XRD should give up due to vanishing diffraction since the hyperfine interactions can still be observed, and sometimes the differences, as compared to the bulk interactions, provide relevant information on the local atomic disorder and local irregularities in the lattice/electron structure, the source of amorphicity.

Among the various types of iron oxides and oxyhydroxides, ferrhydrite ($\text{Fe}^{3+}_{10}\text{O}_{14}(\text{OH})_2$) is the typical amorphous iron hydroxide that has two-line and six-line „polymorphs” referring to the number of diffraction lines showing up in its powder XRD patterns. Here the great variability of the water content causes the amorphous character [42]. A general review of all possible amorphous iron oxides is given in [43].

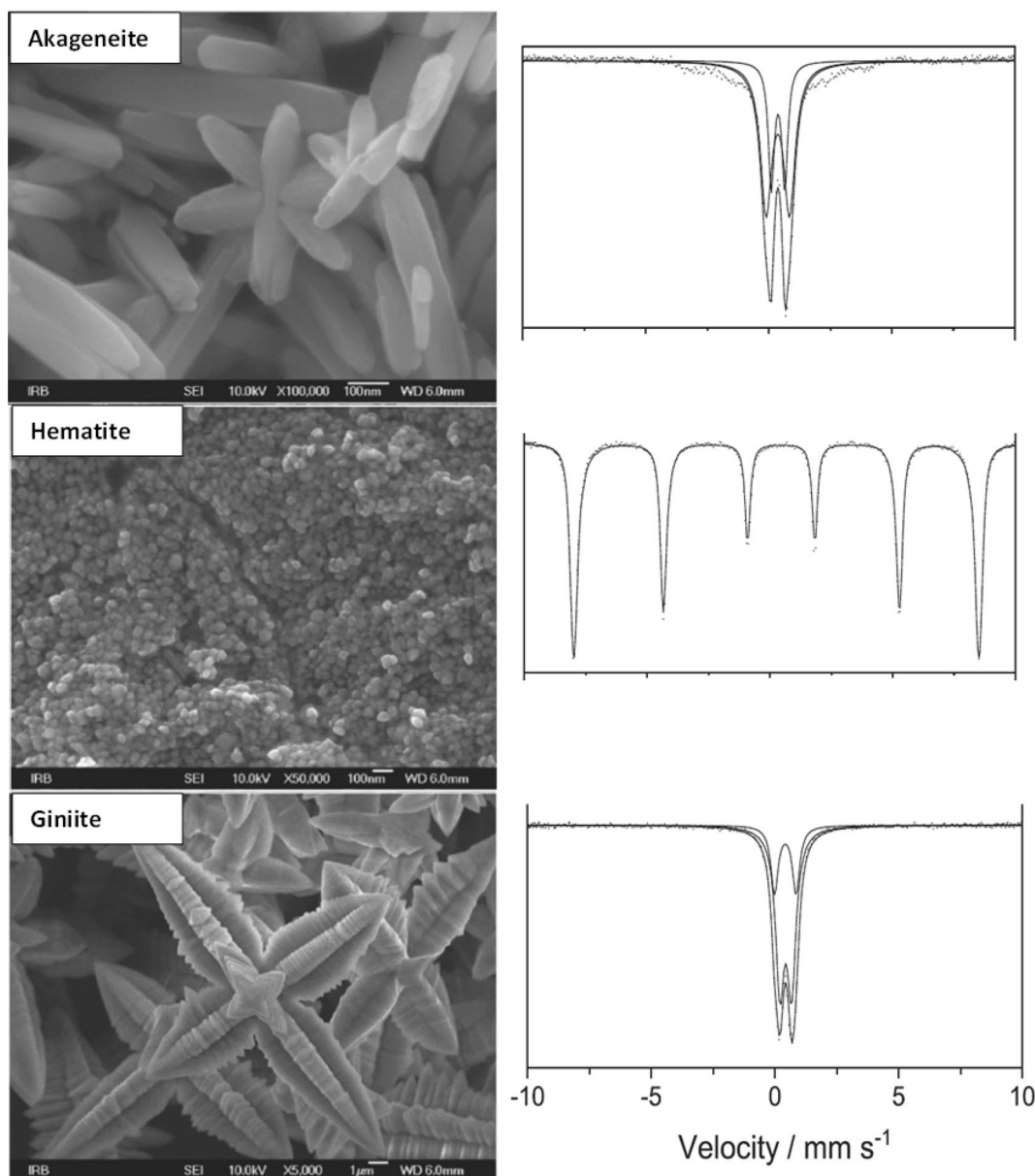


Figure 3: Various iron oxide/oxyhydroxide/phosphate phases produced by forced hydrolysis and their Mössbauer patterns. (Combined and redrawn from Figures in ref. [36].

Silicate glass is automatically assigned to amorphous materials due to the large variability of the connections between the oxygen polyhedra of the glass forming element (for example, [SiO₄] units) without substantial energy difference. Thus quite random short range spatial structures can get frozen leaving no chance for regular XRD patterns. There are various types of such glasses with applications from catalysts to anode materials in novel Li ion batteries [44–48].

The amorphous state is probably most exciting in metallic systems. For metals, the lattice is composed of identical charges (positive ions), therefore defects form easily causing no

unendurable energy states, therefore they move also easily, get annealed, and when frozen, there exists a short range order more or less distorted. Concentrating on iron, mostly some added partner is needed to form an amorphous state (e.g., phosphorous, carbon, boron) and even in such a case, extremely fast cooling is required to freeze an amorphous state (typically rapid quenching with a cooling rate of about 10⁶ K/s) [49–52].

Most amorphous metallic alloys can be produced by the melt spinning technique that provides extreme fast cooling and results in thin ribbons (about 20–30 μm) of the metallic glass. Due to its local atomic sensitivity, Mössbauer spectrometry was

widely applied to these materials in the seventies and eighties. Indeed, it was a very efficient technique providing relevant information on the local structural order around the Fe probe, established from the hyperfine field distribution to be compared with that observed in crystalline alloys having similar compositions [53] and on the orientation of Fe magnetic moments correlated to the quenching conditions (magnetic texture) [54]. Then, Yoshizawa et al. [55] discovered nanocrystalline alloys obtained from amorphous alloys showing two crystallization peaks, subsequently annealed, giving rise to unusual two-phase materials containing nanocrystalline grains embedded in the amorphous remainder; their respective contents strongly depend on the annealing time and temperature (between the two crystallization peaks). These materials (e.g., NANOPERM, HITPERM, FINEMET) show excellent soft magnetic properties combined with high saturation magnetic flux with high permeability, which makes them promising for industrial applications. These magnetic properties and their evolution with temperature have been clearly understood from Mössbauer spectrometry studies at different temperature well-suited to distinguish the respective evolutions of the nanocrystalline grains, the amorphous remainder and even the interface, as well as the nature of the interactions between these different domains [56–59].

One may want to produce nano-sized particles from the ribbon, which is very brittle but grinding would not result in nanoparticles. A popular technique is the electric explosion of the amorphous ribbon when a high current pulse is applied to the wire in water or other liquid. The pulse means kilo amperes in a few microseconds. The ribbon melts and partly evaporates during this time and the question is under what condition the amorphous state can be preserved. A related work is presented in this issue as an example of the application of Mössbauer Spectrometry in this field.

The nanoscale does not necessarily mean three dimensional structures. The thickness of a thin layer may also fall in the nanometer range, and such thin films are essential in the solid state devices used in microelectronics and informatics.

The preparation of thin films requires quite sophisticated techniques such as laser ablation, pulsed laser deposition, magnetron sputtering, etc., and specific conditions such as ultra high vacuum, extremely pure elementary atomic species. In addition, there is a strong need to control the phase composition, crystal growth and especially the required orientation of the crystallites on the surface is crucial, and thus the required chemical and crystallographic nature of the substrate. Mössbauer Spectrometry and sometimes in situ Mössbauer Spectrometry are very helpful in this regard, taking advantage of the dependence of the relative intensities of the sextet lines on the magnetic orientation of Fe moments or magnetic domains [54, 60–62].

Since bulk properties are not expected and this is particularly true for the magnetic structure near the surface regions

of the nano-object, even if the thin layer has only one well-defined phase, the hyperfine magnetic field would not be a single value but will have a distribution. The appropriate computer evaluation methods have been developed [63] and distribution fits are readily accessible today. As an example, a study on the influence of thermal treatment on the crystal growth of a $\text{SrFe}_{12}\text{O}_{19}$ thin film previously deposited on a silicon substrate using radio frequency (RF) magnetron sputtering is the subject in this special issue. The preparation of nanoparticles is usually achieved by hindering/stopping crystal growth when the given phase is formed in a chemical reaction or phase transformation by an appropriate method such as surfactants that cover the surface of the crystallites or simply by fast quenching. The question arises as to how it might be possible to prepare nanoparticles from bulk material. Among the grinding methods, high energy ball milling is currently an applied method, but it has its own limitations.

An even more interesting question is whether metallic iron may be milled into such fine grains that the long range ferromagnetic order would be lost and paramagnetic metallic iron could be observed. Since it is well-established that alloying elements can facilitate this process [64–66], the question of whether pure iron can really be paramagnetic and amorphous remains unanswered. A rather sophisticated „grinding” method is when an electrodeposited pure thin layer of metallic iron is bombarded with heavy particles. If the energy is such that the particles are not stopped in the iron layer, but transmitted only creating defects, the purity in the metallic iron phase can be retained while the defects created by the transmission virtually slice up the thin layer. If the layer is thin enough, a situation can be witnessed where the unperturbed (non-irradiated) iron shows magnetic splitting because the long range magnetic interaction for ferromagnetic coupling is given in 2 dimensions, but once the irradiation takes place, the small domains created may lose the ferromagnetic coupling and the metallic iron will show up as a paramagnetic doublet in the Mössbauer spectrum. A successful experiment of such type is reported in this Focus Issue.

As discussed earlier, soils can contain naturally formed nanometer sized particles of some iron oxyhydroxides and oxides that play an important role in iron metabolism in plants, and have been studied by Mössbauer Spectrometry by several research groups [67–71]. Ferritin, as a general iron storage organelle in cells is important not only for plants and its Mössbauer study is quite challenging because ferritin particles are nanometer sized and are amorphous [72, 73].

Some organic ligands play very important role in the iron metabolism, and citrate seems to be the number one in this series. Interaction between citric acid and iron has been thoroughly studied and still it is not a fully explored area of research (Figure 4, [74]).

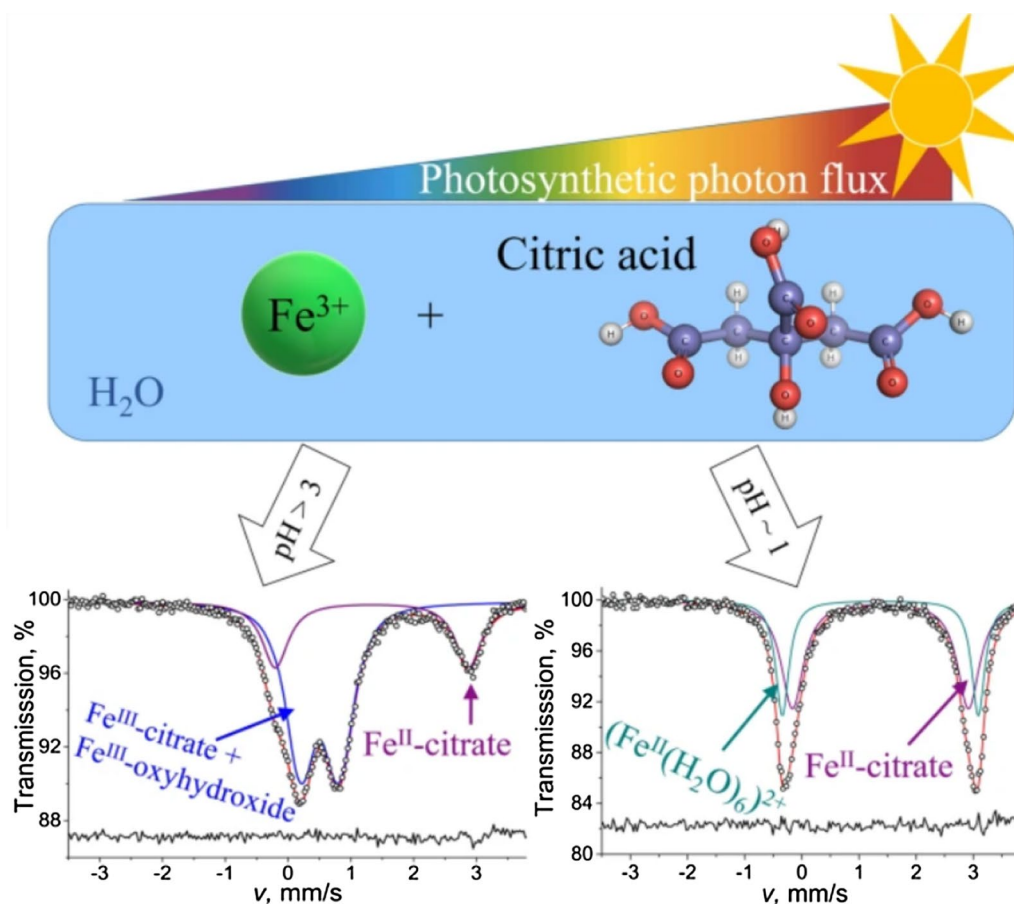


Figure 4: Demonstration of the pH-dependence of the citric acid-related iron species crucial for iron metabolism in plants under photochemical influence [74].

The source of iron for plants in the soil is definitely the iron oxyhydroxides and oxides available there, regardless of the organic ligand that may be involved in the transport process. Nanoparticles have the advantage of a faster dissolution ability than that of bulk mineral grains but not too fast dissolution rate (as with normal iron salts) that would allow the iron to be removed before uptake by the plant. Thus these nanoparticles can be considered as fertilizers [75, 76]. This research area is also involved in this Focus Issue.

One of the interesting areas in the material science is metal-organic frameworks (MOFs), which have applications ranging from sensing to energy to environment due to their porous structural properties [77–79]. MOFs consist of organic ligands linked to metallic cations. MIL-53 as an example of MOFs in this special issue, which is $M^{III}(\mu_2\text{-OH})(\text{BDC})$ (BDC = 1,4-benzenedicarboxylate), possessing chains of corner-sharing MO_6 octahedra connected through the organic ditopic ligands (crystal structure of MIL-53 is shown in Figure 5 [80]).

The research presented in the article showed how Mössbauer spectrometry in conjunction with X-ray spectrometry can be applied to gain insight in-depth information on accurate

description of the complex mesoporous hybrid like MIL-53, to check the number of Fe sites, the thermal stability of the structure and the content of water in the pores.

Researcher have contributed to the issue on the synthesis of magnetic solution in which aluminum ion was partially replaced from calcium hexaluminate (CA6) with iron ion ($\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ ternary system) [81]. Preparation of such solution is challenging and Mössbauer spectrometry was able to assist researchers to maximize the iron content in the ternary solution in order to obtain its magnetic properties.

In the seventies and eighties, various methods were developed to synthesize a wide variety of crystalline and amorphous ferric and ferrous fluorides [82] which were systematically studied by Mössbauer spectrometry [83]. Much attention was paid to ferric fluorides to calculate the electric field gradients at Fe site using a point charge model [84] and to correlate structural and magnetic properties. Indeed, unusual magnetic structures resulting from the cationic topology combined with the presence of antiferromagnetic interactions were found to be non-collinear due to the presence of frustrated magnetic interactions, particularly the different crystalline, amorphous and nanostructured

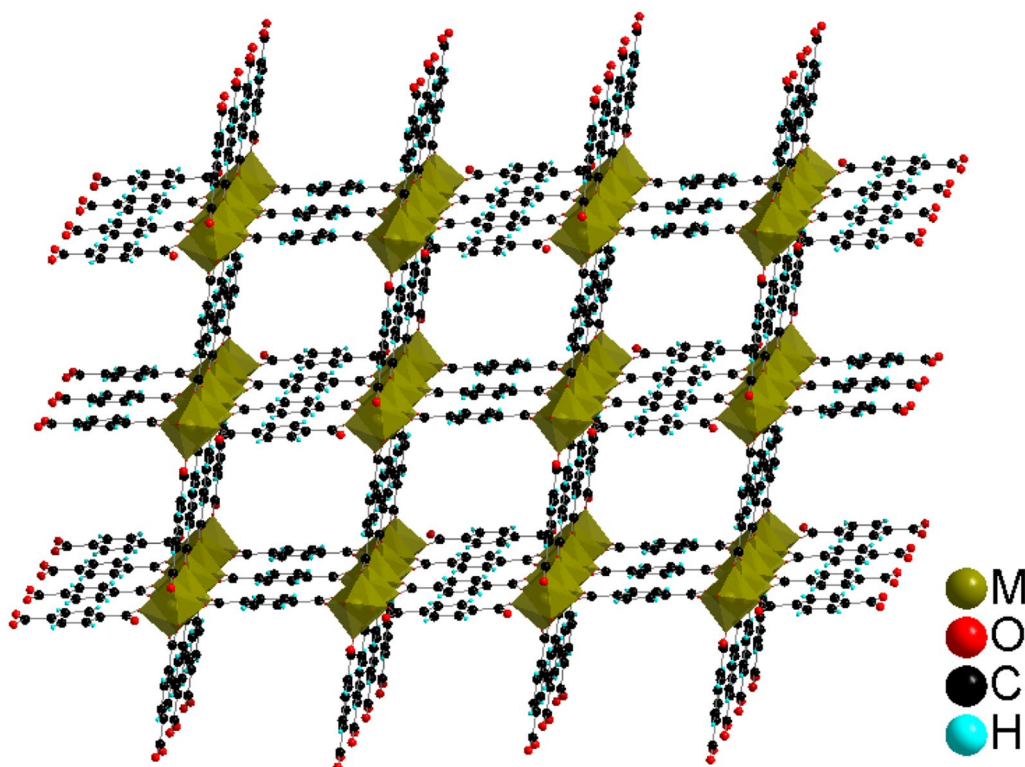


Figure 5: Crystal structure of MIL-53(M). Top: inorganic chain; bottom: full crystal structure, view along the channels axis.

phases of FeF_3 which shows an fascinating polymorphism [83]. One of the interesting article in the special issue was on the synthesis of iron-based fluorides, anhydrous, hydrates or hybrids i.e., conversion of $((\text{NH}_4)\text{CuFeF}_6$ to the hydrate $(\text{NH}_4)\text{CuFeF}_6(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$. Such compounds have properties suitable for optics, microelectronics, and catalytical applications [85–87]. Importantly, ^{57}Fe Mössbauer spectrometry was able to explain in detail the chemical compositions and highlighted the anionic and/or cationic orders or disorders. This type of mechanistic study may allow the preparation of nanoparticles to perform electrochemical studies.

The application of Mössbauer spectrometry has also been shown in the synthesis of an environmental material that could degrade pollutants such as dyes [88–93]. In this research, this material was a composite of zeolite and iron oxide, and the authors were able to apply this local probe technique to study the nucleation of goethite ($\alpha\text{-FeOOH}$) in the composite. The presence of the zeolite allowed to have visible light absorption of the composite, which contributed to the degradation of the targeted dye.

Another example of the application of Mössbauer spectrometry in the synthesis and characterization of environmental material is the synthesis of magnesium ferrite-bentonite nanocomposite that can produce visible light active photocatalysts to degrade pesticides and industrial pollutants in water [

Bentonite (two building units i.e., silicon-oxygen tetrahedron $[\text{Si}_2\text{O}_5]^{2-}$ and aluminum octahedron $[\text{Al}(\text{OH})_6]^{3-}$) could provide catalytic active sites to prevent the aggregation of ferrite nanoparticles to enhance the surface area of the synthesized nanocomposite. The interaction between bentonite and magnesium ferrite was examined by Mössbauer spectrometry and X-ray photoelectron spectroscopy in order to produce highly efficient photocatalyst. The important finding of the synthesized nanocomposite was to demonstrate the synergistic remediation of toxic metal ions and organic pollutants in water.

Data availability

These are available upon request.

Declarations

Conflict of interest The authors declare no competing financial interest.

References

1. E. Bill, Editor(s): R. R. Crichton, R. O. Louro, ^{57}Fe -Mössbauer spectroscopy and basic interpretation of Mössbauer

- parameters, Practical Approaches to Biological Inorganic Chemistry (Second Edition), Elsevier, p. 201–208 (2020). <https://doi.org/10.1016/B978-0-444-64225-7.00006-7>.
2. Y. Zeng, X. Li, J. Wang, Y. Huang, T. Zhang, B. Liu, In situ/operando Mössbauer spectroscopy for probing heterogeneous catalysis. *Chem. Catalysis*. **1**, 1215 (2021). <https://doi.org/10.1016/j.checat.2021.08.013>
3. J. Zhang, X. Tang, H. Yi, Q. Yu, Y. Zhang, J. Wei, Y. Yuan, Synthesis, characterization and application of Fe-zeolite: a review. *Appl. Catal. A* **630**, 118467 (2022). <https://doi.org/10.1016/j.apcata.2021.118467>
4. X. Li, K. Zhu, J. Pang, M. Tian, J. Liu, A.I. Rykov, M. Zheng, X. Wang, X. Zhu, Y. Huang, B. Liu, J. Wang, W. Yang, T. Zhang, Unique role of Mössbauer spectroscopy in assessing structural features of heterogeneous catalysts. *Appl. Catal. B* **224**, 518 (2018). <https://doi.org/10.1016/j.apcatb.2017.11.004>
5. M. Gracheva, Z. Homonnay, K. Kovács, K.A. Béres, J.C. Biondi, Y. Wenchao, V.K. Kis, M. Polgári, Mössbauer characterization of microbially mediated iron and manganese ores of variable geological ages. *Ore Geol. Rev.* **134**, 104124 (2021). <https://doi.org/10.1016/j.oregeorev.2021.104124>
6. O. Castelein, L. Aldon, J. Olivier-Fourcade, J.C. Jumas, J.P. Bonnet, P. Blanchart, ^{57}Fe Mössbauer study of iron distribution in a kaolin raw material: influence of the temperature and the heating rate. *J. Eur. Ceram. Soc.* **22**, 1767 (2002). [https://doi.org/10.1016/S0955-2219\(01\)00496-4](https://doi.org/10.1016/S0955-2219(01)00496-4)
7. E. Di Iorio, L. Circelli, R. Angelico, J. Torrent, W. Tan, C. Colombo, Environmental implications of interaction between humic substances and iron oxide nanoparticles: a review. *Chemosphere* **303**, 135172 (2022). <https://doi.org/10.1016/j.chemosphere.2022.135172>
8. B.F. Costa, E.I. Alves, P.A. Silva, A.C. Batista, ^{57}Fe Mössbauer Analysis of Meteorites and Tektites. *Minerals* **11**, 628 (2021). <https://doi.org/10.3390/min11060628>
9. Y. Hu, F. Li, C. Liu, K. Rosso, Z. Shi, Iron redox chemistry and its environmental impact a virtual special issue. *ACS Earth Space Chem.* **3**, 2374 (2019). <https://doi.org/10.1021/acsearthspacechem.9b00282>
10. J. Yuan, Y. Wen, D.D. Dionysiou, V.K. Sharma, X. Ma, Biochar as a novel carbon-negative electron source and mediator: electron exchange capacity (EEC) and environmentally persistent free radicals (EPFRs): a review. *Chem. Eng. J.* **429**, 132313 (2022). <https://doi.org/10.1016/j.cej.2021.132313>
11. J.W.G. Wignall, Mössbauer Line Broadening in Trivalent Iron Compounds. *J. Chem. Phys.* **44**, 2462 (1966)
12. R.M. Housley, Investigation of Magnetic Relaxation Effects in $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ by Mössbauer-Effect Spectroscopy. *J. Appl. Phys.* **38**, 1287 (1967)
13. A.J. Nozik, M. Kaplan, Paramagnetic and Electric Quadrupole Hyperfine Interactions of Ferric Ions in Ice and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. *J. Chem. Phys.* **49**, 4141 (1968)
14. U. Russo, S. Calogero, N. Burriesci, M. Petrera, Mössbauer characterization of some new high-spin iron complexes with urea and thiourea derivatives. *J. Inorg. Nucl. Chem.* **41**, 25 (1979)
15. S. Calogero, U. Russo, A. Del Pra, Characterization of some high-spin iron(III) complexes with urea derivatives. Crystal structure of diaquatetrakis(perhydropyrimidin-2-one)iron trichloride dihydrate and of perhydropyrimidin-2-one. *J. Chem. Soc. Dalton Trans.* **4**, 646 (1980)
16. S. Yamauchi, Y. Sakai, T. Tominaga, Paramagnetic relaxation effects on Mössbauer spectra of hexakis(alkylurea)iron(III) complexes. *J. Radioanal. Nucl. Chem. Lett.* **119**, 283 (1987)
17. S. Yamauchi, Y. Sakai, H. Nishioji, T. Tominaga, Mössbauer spectroscopic study of the magnetic relaxation in tris(β -diketonato)iron(III) complexes. *Int. J. Appl. Radiat. Isot.* **34**, 977 (1983)
18. G. Galeazzi, U. Russo, G. Valle, S. Calogero, Mössbauer study of some iron(III) complexes with urea type ligands and the crystal structure of hexakisdimethylureairon(III) perchlorate. *Transition Met. Chem.* **6**, 325 (1981)
19. K.A. Béres, Z. Homonnay, L. Kvitek, Z. Dürvanger, M. Kubikova, V. Harmat, F. Szilágyi, Z. Czégény, P. Németh, L. Bereczki, V.M. Petruševski, M. Pápai, A. Farkas, L. Kótai, Thermally-induced solid-phase quasi-intramolecular redox reactions of [hexakis(urea-O)iron(III)] permanganate: an easy way to prepare $(\text{Fe}, \text{Mn})\text{O}_x$ catalysts for CO_2 hydrogenation. *Inorg. Chem.* **61**, 14403 (2022). <https://doi.org/10.1021/acs.inorgchem.2c02265>
20. R.M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions and Uses*, 2nd edn. (Wiley, Weinheim, 2003)
21. S. Wu, A. Sun, F. Zhai, J. Wang, W. Xu, Q. Zhang, A.A. Volinsky, Fe_3O_4 magnetic nanoparticles synthesis from tailings by ultrasonic chemical co-precipitation. *Mater. Lett.* **65**, 1882 (2011). <https://doi.org/10.1016/j.matlet.2011.03.065>
22. M. Sasidharan, H.N. Luitel, N. Gunawardhana, M. Inoue, S.I. Yusa, T. Watari, K. Nakashima, Synthesis of magnetic $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 hollow nanospheres for sustained release of ibuprofen. *Mater. Lett.* **73**, 4 (2012). <https://doi.org/10.1016/j.matlet.2011.12.058>
23. P. Yang, A. Zhang, X. Cheng, G. Zhou, M. Lü, Morphology-tunable fibers with Fe_3O_4 nanocrystals fabricated through assembly. *J. Colloid Interface Sci.* **351**, 77 (2010). <https://doi.org/10.1016/j.jcis.2010.07.041>
24. Q. Gao, F. Chen, J. Zhang, G. Hong, J. Ni, X. Wei, D. Wang, The study of novel $\text{Fe}_3\text{O}_4@ \gamma\text{-Fe}_2\text{O}_3$ core/shell nanomaterials with improved properties. *J. Magn. Magn. Mater.* **321**, 1052 (2009). <https://doi.org/10.1016/j.jmmm.2008.10.022>
25. S. Musić, M. Ristić, S. Krehula, ^{57}Fe Mössbauer spectroscopy in the investigation of the precipitation of iron oxides, in *Mössbauer Spectroscopy: Applications in Chemistry, Biology and Nanotechnology*, ed. by V.K. Sharma, G. Klingelhöfer, T. Nishida, (Wiley, 2013), pp. 470–504. <https://doi.org/10.1002/9781118714614.ch23>.
26. J.-M. Greneche. The Contribution of ^{57}Fe Mössbauer Spectrometry to Investigate Magnetic Nanomaterials. In *Mössbauer*

- Spectroscopy, ed. by Yutaka Yoshida and Guido Langouche. pp.187–241. Springer, Berlin (2013) and references therein
27. W. Kündig, R.S. Hargrove, Electron hopping in magnetite. *Solid State Commun.* **7**, 223–227 (1969). [https://doi.org/10.1016/0038-1098\(69\)90729-7](https://doi.org/10.1016/0038-1098(69)90729-7)
 28. A.C. Doriguetto, N.G. Fernandes, A.I.C. Persiano, E. Nunes Filho, J.-M. Grenèche, J.D. Fabris, Characterization of a natural magnetite. *Phys. Chem. Minerals* **30**, 249 (2003). <https://doi.org/10.1007/s00269-003-0310-x>
 29. W. Ramadan, M.I. Zaki, N.E. Fouad, G.A.H. Mekhemer, Particle characteristics and reduction behavior of synthetic magnetite. *J. Magn. Magn. Mater.* **355**, 246 (2014). <https://doi.org/10.1016/j.jmmm.2013.12.006>
 30. T.J. Daou, S. Begin-Colin, J.-M. Grenèche, F. Thomas, A. Derory, P. Bernhardt, P. Legare, G. Pourroy, Phosphate Adsorption Properties of Magnetite-Based Nanoparticles. *Chem. Mater.* **19**, 4494 (2007). <https://doi.org/10.1021/cm071046v>
 31. T.J. Daou, J.-M. Grenèche, G. Pourroy, S. Buathong, A. Derory, C. Ulhaq-Bouillet, B. Donnio, D. Guillon, S. Begin-Colin, Coupling agent effect on magnetic properties of functionalized magnetite-based nanoparticles. *Chem. Mater.* **20**, 5869 (2008). <https://doi.org/10.1021/cm801405n>
 32. M.A. Shipilin, I.N. Zakharova, A.M. Shipilin, V.I. Bachurin, Mössbauer studies of magnetite nanoparticles. *J. Surf. Investig. X-ray Synchrotron. Techn.* **8**, 557 (2014). <https://doi.org/10.1134/S1027451014030343>
 33. J.S. Salazar, L. Perez, O. de Abril, L.T. Phuoc, D. Ihiwakrim, M. Vazquez, J.M. Grenèche, S. Begin-Colin, G. Pourroy, Magnetic Iron Oxide Nanoparticles in 10–40 nm Range: Composition in Terms of Magnetite/Maghemite Ratio and Effect on the Magnetic Properties. *Chem. Mater.* **23**, 1379 (2011). <https://doi.org/10.1021/cm060805r>
 34. L.K. Bogart, J. Fock, G.M. da Costa, K. Witte, J.-M. Grenèche, J. Zukrowski, M. Sikora, D.E. Latta, M.M. Scherer, M. Fougat Hansen, C. Frandsen, Q.A. Pankhurst, Prenormative verification and validation of a protocol for measuring magnetite–maghemite ratios in magnetic nanoparticles. *Metrologia* **59**, 015001 (2022). <https://doi.org/10.1088/1681-7575/ac36b6>
 35. E. Tronc, P. Prené, J.P. Jolivet, J.L. Dormann, J.M. Grenèche, Spin-canting in γ -Fe₂O₃ Nanoparticles. *Hyperfine Interact.* **112**, 97 (1997)
 36. M. Robic, M. Ristic, S. Krehula, S. Music, Forced hydrolysis of FeCl₃ solutions in the presence of guanylurea phosphate. *Colloids Surf. A* **634**, 128047 (2022). <https://doi.org/10.1016/j.colsurfa.2021.128047>
 37. R.E. Vandenberghe and E. De Grave, Application of Mössbauer Spectroscopy. In *Earth Sciences. in Mössbauer Spectroscopy*, ed. by Yutaka Yoshida and Guido Langouche, pp. 91–185. Springer, Berlin (2013) and references therein
 38. J.W. Stucki, B.A. Goodman, U. Schwertmann, *Iron in soils and clay minerals* (D. Riedel Publishing Company, Dordrecht, 1988)
 39. A.L. Irshinskii, V.M. Cherepanov, *Sov. Phys. JETP* **51**, 644 (1980)
 40. E. Murad, J. Cashion, *Mössbauer Spectroscopy of Environmental Materials and Their Industrial Utilization* (Springer, New York, 2004)
 41. J. M. D. Coey, Magnetic Properties of Iron in Soil Iron Oxides and Clay Minerals In: J.W. Stucki, B.A. Goodman, U. Schwertmann (eds): *Iron in Soils and Clay Minerals*, NATO ASI Series, 217, Springer, Dordrecht. (1988). https://doi.org/10.1007/978-94-009-4007-9_14.
 42. R.J. Pollard, C.M. Cardile, D.G. Lewis, L.J. Brown, Characterization of FeOOH polymorphs and ferrihydrite using low-temperature, applied-field Mössbauer spectroscopy. *Clay Miner.* **27**, 57 (1992). <https://doi.org/10.1180/claymin.1992.027.1.06>
 43. L. Machala, R. Zboril, A. Gedanken, Amorphous iron (III) oxide a review. *J. Phys. Chem. B* **111**, 4003 (2007). <https://doi.org/10.1021/jp064992s>
 44. T. Nishida, S. Kubuki, N. Oka, Local structure, glass transition, structural relaxation, and crystallization of functional oxide glasses investigated by Mössbauer spectroscopy and DTA. *J. Mater. Sci. Mater. Electronics* **32**, 23655 (2021). <https://doi.org/10.1007/s10854-021-06855-w>
 45. F.J. Litterst, Mössbauer studies of crystallization, glass transition and structural relaxation in non-metallic amorphous materials. *Nucl. Instrum. Methods Phys. Res.* **199**, 87 (1982). [https://doi.org/10.1016/0167-5087\(82\)90179-X](https://doi.org/10.1016/0167-5087(82)90179-X)
 46. J.M.D. Coey, Amorphous Solids: A Review of the Applications of the Mössbauer Effect. *J. Phys. Colloques* **35**, C6-89 (1974). <https://doi.org/10.1051/jphyscol:1974608>
 47. L. Lv, M. Peng, L. Wu, Y. Dong, G. You, Y. Duan, W. Yang, L. He, X. Liu, Progress in Iron Oxides Based Nanostructures for Applications in Energy Storage. *Nanoscale Res Lett* **16**, 138 (2021). <https://doi.org/10.1186/s11671-021-03594-z>
 48. X. Wang, X. Zhang, Y. Zhang, Y. Wang, S.-P. Sun, W.D. Wua, Z. Wu, Nanostructured semiconductor supported iron catalysts for heterogeneous photo-Fenton oxidation: a review. *J. Mater. Chem. A* **8**, 15513 (2020). <https://doi.org/10.1039/D0TA04541A>
 49. C. Suryanarayana, A. Inoue, Iron-based bulk metallic glasses. *Int. Mater. Rev.* **58**, 131 (2013). <https://doi.org/10.1179/1743280412Y.0000000007>
 50. K. Brzózka, A. Ślowska-Waniewska, K. Jezuita, Mössbauer studies of FeZrB(Cu) amorphous alloys. *J. Magn. Magn. Mater.* **160**, 255 (1996). [https://doi.org/10.1016/0304-8853\(96\)00186-2](https://doi.org/10.1016/0304-8853(96)00186-2)
 51. S.M. Fries, H.-G. Wagner, U. Gonser, L. Schlappbach, R. Montiel-Montoya, Mössbauer investigations of the changes in the magnetic properties of amorphous iron rich Fe-Zr alloys with hydrogenation. *J. Magn. Magn. Mater.* **45**, 331 (1984). [https://doi.org/10.1016/0304-8853\(84\)90027-1](https://doi.org/10.1016/0304-8853(84)90027-1)
 52. A. Amamou, Mössbauer Effect and Short-Range Order in Fe-P-B and Fe-P-C Amorphous Alloys. *Phys. Status Solidi* **54**, 565 (1979). <https://doi.org/10.1002/pssa.2210540217>

53. U. Gonser, R. Preston, Mössbauer spectroscopy applied to amorphous metals. *Top. Appl. Phys.* **53**, 93 (1983)
54. J.-M. Greneche, F. Varret, On the texture problem in Mössbauer Spectroscopy. *J. Phys. C: Solid State Phys.* **15**, 5333 (1982)
55. Y. Yoshizawa, K. Yamauchi, Fe-based soft magnetic alloys composed of ultrafine grain structure. *Mater. Trans. JIM* **31**, 307 (1990)
56. J.-M. Greneche, M. Miglierini, Mössbauer spectrometry applied to iron-based nanocrystalline alloys: I High temperature studies. *Mössbauer Spectroscopy in Materials Science*, M. Miglierini and D. Petridis (eds.) Kluwer Academic Publishers, Dordrecht (1999) pp. 243–256 and references therein.
57. M. Miglierini, J.-M. Greneche, Mössbauer spectrometry applied to iron-based nanocrystalline alloys: I Hyperfine field distributions. *Mössbauer Spectroscopy in Materials Science*, M. Miglierini and D. Petridis (eds.) Kluwer Academic Publishers, Dordrecht (1999) pp. 257–272 and references therein.
58. M. Kopcewicz, Mössbauer study of nanocrystalline alloys. *Acta Physica Polonica* **96**, 49 (1999)
59. T. Kemény, D. Kaptás, L.F. Kiss, J. Balogh, I. Vincze, S. Szabó, D.L. Beke, Structure and magnetic properties of nanocrystalline soft ferromagnets. *Hyperfine Interact.* **130**, 181 (2000) (and references therein)
60. E. Kuzmann, I. Felner, L. Szirák, S. Stichleutner, Z. Homonnay, M.R. El-Sharif, C.U. Chisholm, Magnetic anisotropy and microstructure in electrodeposited quaternary Sn-Fe-Ni-Co alloys with amorphous character. *Materials* **15**, 3015 (2022). <https://doi.org/10.3390/ma15093015>
61. R.A. Nazipov, R.I. Batalov, R.M. Bayazitov, H.A. Novikov, V.A. Shustov, E.N. Dulov, High-intensity pulsed ion beam treatment of amorphous iron-based metal alloy. *J. Phys. Conf. Ser.* **1588**, 012039 (2020). <https://doi.org/10.1088/1742-6596/1588/1/012039>
62. T. Funabashi, Y. Kobayashi, Y. Yamada, Metastable iron carbide thin films produced by pulsed laser deposition of iron in methane atmosphere. *Hyperfine Interact* **240**, 121 (2019). <https://doi.org/10.1007/s10751-019-1668-6>
63. P. Mangin, G. Marchal, M. Piecuch, C. Janot, Mossbauer spectra analysis in amorphous system studies. *J. Phys. E: Sci. Instrum.* **9**, 1101 (1976). <https://doi.org/10.1088/0022-3735/9/12/025>
64. J. Logan, E. Sun, A Mössbauer study of amorphous iron-phosphorus alloys. *J. Non-Cryst. Solids* **20**, 285 (1976). [https://doi.org/10.1016/0022-3093\(76\)90137-X](https://doi.org/10.1016/0022-3093(76)90137-X)
65. Y.Z. Zhang, L.H. Zhe, X.Z. Du, R.M. Yang, R. Xu, Thermal stability and microstructure of the electrodeposited amorphous Fe₈₀P₁₈Yb₂ alloy. *J. Non-Cryst. Solids* **117–118**, 259 (1990). [https://doi.org/10.1016/0022-3093\(90\)90928-F](https://doi.org/10.1016/0022-3093(90)90928-F)
66. Z. Hu, Y. Chen, Y. Hsia, Ultrafine amorphous Fe-Ni-B and Fe-P-B particles. *Nucl. Instrum. Methods Phys. Res. Sect. B* **76**, 121 (1993). [https://doi.org/10.1016/0168-583X\(93\)95154-W](https://doi.org/10.1016/0168-583X(93)95154-W)
67. A. A. Kamnev, K. Kovacs, I. V. Alenkina, M. I. Oshtrakh, Mössbauer spectroscopy in biological and biomedical research. *Mössbauer Spectroscopy*, eds: V. K. Sharma, G. Klingelhöfer, T. Nishida, Wiley, (2013) pp. 272–291, <https://doi.org/10.1002/9781118714614.ch13>.
68. K. Kovács, E. Kuzmann, F. Fodor, E. Cseh, Z. Homonnay, A. Vértes (2008) Mössbauer investigation of iron uptake in wheat. In ICAME 2007, ed. by N.S. Gajbhiye, S.K. Date, Springer, Berlin. pp. 743–747. https://doi.org/10.1007/978-3-540-78697-9_101.
69. K. Kovács, E. Kuzmann, E. Tatár, A. Vértes, F. Fodor, Investigation of iron pools in cucumber roots by Mössbauer spectroscopy: direct evidence for the Strategy I iron uptake mechanism. *Planta* **229**, 271 (2009). <https://doi.org/10.1007/s00425-008-0826-x>
70. K. Kovács, E. Kuzmann, A. Vértes, L. Lévai, E. Cseh, F. Fodor, Effect of cadmium on iron uptake in cucumber roots: a Mössbauer-spectroscopic study. *Plant Soil* **327**, 49 (2010). <https://doi.org/10.1007/s11104-009-0030-1>
71. S.H. Kilcoyne, P.M. Bentley, P. Thongbai, D.C. Gordon, B.A. Goodman, The application of ⁵⁷Fe Mössbauer spectroscopy in the investigation of iron uptake and translocation in plants. *Nucl. Instrum. Methods Phys. Res., Sect. B* **160**, 157 (2000). [https://doi.org/10.1016/S0168-583X\(99\)00579-0](https://doi.org/10.1016/S0168-583X(99)00579-0)
72. P.M. Proulx-Curry, N.D. Chasteen, Molecular aspects of iron uptake and storage in ferritin. *Coord. Chem. Rev.* **144**, 347 (1995). [https://doi.org/10.1016/0010-8545\(95\)01148-1](https://doi.org/10.1016/0010-8545(95)01148-1)
73. G.C. Papaefthymiou, The Mössbauer and magnetic properties of ferritin cores. *Biochim. Biophys. Acta* **1800**, 886 (2010). <https://doi.org/10.1016/j.bbagen.2010.03.018>
74. M. Gracheva, Z. Homonnay, A. Singh, F. Fodor, V.B. Marosi, Á. Solti, K. Kovács, New aspects of the photodegradation of iron(III) citrate: spectroscopic studies and plant-related factors. *Photochem. Photobiol. Sci.* **21**, 983 (2022). <https://doi.org/10.1007/s43630-022-00188-1>
75. J. Carrasco, K. Kovács, V. Czech, F. Fodor, J.J. Lucena, A. Vértes, L. Hernández-Apaolaza, Influence of pH, iron source, and Fe/ligand ratio on iron speciation in lignosulfonate complexes studied using Mössbauer Spectroscopy. Implications on their fertilizer properties. *J. Agric. Food Chem.* **60**, 3331 (2012). <https://doi.org/10.1021/jf204913s>
76. P. Lemanceau, P. Bauer, S. Kraemer, J.F. Briat, Iron dynamics in the rhizosphere as a case study for analyzing interactions between soils, plants and microbes. *Plant Soil* **321**, 513 (2009). <https://doi.org/10.1007/s11104-009-0039-5>
77. Y. Wen, Á. Rentería-Gómez, G.S. Day, M.F. Smith, T.-H. Yan, R.O.K. Ozdemir, O. Gutierrez, V.K. Sharma, X. Ma, H.-C. Zhou, Integrated photocatalytic reduction and oxidation of perfluorooctanoic acid by metal–organic frameworks: key insights into

- the degradation mechanisms. *J. Am. Chem. Soc.* **144**, 11840 (2022). <https://doi.org/10.1021/jacs.2c04341>
78. M. Feng, P. Zhang, H.-C. Zhou, V.K. Sharma, Water-stable metal-organic frameworks for aqueous removal of heavy metals and radionuclides: A review. *Chemosphere* **209**, 783 (2018). <https://doi.org/10.1016/j.chemosphere.2018.06.114>
 79. G. Férey, Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **37**, 191 (2008). <https://doi.org/10.1039/B618320B>
 80. F. Millange, R.I. Walton, MIL-53 and Its Isoreticular Analogues: A Review of the Chemistry and Structure of a Prototypical Flexible Metal-Organic Framework. *Israel J. Chem.* **58**, 1019 (2018). <https://doi.org/10.1002/ijch.201800084>
 81. B.A. Duell, J. Li, P.G. Labarre, J.J. Zhang, R.P. Hermann, A.P. Ramirez, M.A. Subramanian, Structure and electronic properties of $\text{CaAl}_{12-x}\text{Fe}_x\text{O}_{19}$ hibonites. *J. Solid State Chem.* **291**, 121650 (2020). <https://doi.org/10.1016/j.jssc.2020.121650>
 82. G. Férey, M. Leblanc, R. DePape, J. Pannetier, in *Inorganic Solid Fluorides*. ed. by P. Hagenmuller (Academic Press, New York, 1985)
 83. J.-M. Greneche, F. Varret, Mössbauer effect studies on iron fluorides, Mössbauer Spectroscopy Applied to Magnetism and Materials Science, Edited by G. Long and F. Grandjean, Plenum Press, New-York (1993) pp. 161–203. and references therein.
 84. J. Teillet, Y. Calage, F. Varret, Electric field gradients in AFeIIIIF4 structures: Calculations for the polarizable point charge model and Mössbauer data. *J. Phys. Chem. Solids* **43**, 863 (1982). [https://doi.org/10.1016/0022-3697\(82\)90035-X](https://doi.org/10.1016/0022-3697(82)90035-X)
 85. T. Krah, E. Kemnitz, Aluminium Fluoride - the Strongest Solid Lewis Acid: Structure and Reactivity. *Catal. Sci. Technol.* **7**, 773 (2017). <https://doi.org/10.1039/c6cy02369j>
 86. M. Leblanc, V. Maissoneuve, A. Tressaud, Crystal Chemistry and Selected Physical Properties of Inorganic Fluorides and Oxide-Fluorides. *Chem. Rev.* **115**, 1191 (2015). <https://doi.org/10.1021/cr500173c>
 87. K. Lemoine, A. Hémon-Ribaud, M. Leblanc, J. Lhoste, J.-M. Tarascon, V. Maissoneuve, Fluorinated Materials as Positive Electrodes for Li- and Na-Ion Batteries. *Chem. Rev.* **122**, 14405 (2022). <https://doi.org/10.1021/acs.chemrev.2c00247>
 88. N.J. Singh, B. Wareppam, S. Ghosh, B.P. Sahu, P.K. AjiKumar, H.P. Singh, S. Chakraborty, S.S. Pati, A.C. Oliveira, S. Barg, V.K. Garg, L.H. Singh, Alkali-cation-incorporated and functionalized iron oxide nanoparticles for methyl blue removal/decomposition. *Nanotechnology* **31**, 425703 (2020), <https://doi.org/10.1088/1361-6528/ab9af1>.
 89. M. Kaur, M. Kaur, D. Singh, A.C. Oliveira, V.K. Garg, V.K. Sharma, Synthesis of CaFe_2O_4 -NGO Nanocomposite for Effective Removal of Heavy Metal Ion and Photocatalytic Degradation of Organic Pollutants. *Nanomaterials* **11**(6), 1471 (2021). <https://doi.org/10.3390/nano11061471>
 90. E. Casbeer, V.K. Sharma, X.-Z. Li, Synthesis and photocatalytic activity of ferrites under visible light: a review. *Sep. Purif. Technol.* **87**, 1 (2012). <https://doi.org/10.1016/j.seppur.2011.11.034>
 91. M. Kaur, M. Kaur, D. Singh, M. Feng, V.K. Sharma, Magnesium ferrite-nitrogen-doped graphene oxide nanocomposite: effective adsorptive removal of lead(II) and arsenic(III). *Environ. Sci. Pollut. Res.* **29**, 48260 (2022). <https://doi.org/10.1007/s11356-022-19314-8>
 92. J.K. Grewal, M. Kaur, K. Mandal, V.K. Sharma, Carbon quantum dot-titanium doped strontium ferrite nanocomposite: Visible light active photocatalyst to degrade nitroaromatics. *Catalysts* **12**, 1126 (2022). <https://doi.org/10.3390/catal12101126>
 93. M.K. Ubhi, M. Kaur, D. Singh, M. Javed, A.C. Oliveira, V.K. Garg, V.K. Sharma, Hierarchical Nanoflowers of MgFe_2O_4 , Bentonite and B-, P- Co-Doped Graphene Oxide as Adsorbent and Photocatalyst: Optimization of Parameters by Box-Behnken Methodology. *International Journal of Molecular Science* **23**, 9678 (2022). <https://doi.org/10.3390/ijms23179678>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.