

Study of titanomagnetite sands from Costa Rica

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Abstract

In Cahuita town, Limon province, at the Atlantic coast of Costa Rica there are titanomagnetite sands. The chemical, structural and magnetic characterization of the titanomagnetite sands can clarify aspects of their geological formation; as well as suggest applications from them.

The magnetic sand is composed mainly of titanomagnetite and hematite, with very small quartz impurities quantities, pyroxene, etc. The refinement of X-rays diffraction patterns by the method of Rietveld indicates an 86.03% in weight of titanomagnetite and a 13.97% in weight of hematite. The particles size of this magnetic sand have an interval of 75–300 μm and a specific surface area of 1.18 m^2/g . The specific magnetization of the saturation of the sand is 55.8 emu/g and the intrinsic coercivity is 39.6 Oe.

In this work a characterization of the titanomagnetite sands is presented the chemical composition was determined by absorption spectroscopy. The present crystalline phases were determined by X-ray diffraction. The morphology and composition of the particles were determined by scanning electron microscopy together with microanalytical techniques. The classification of the particles by shape and color were carried out using optical microscopy. The magnetic properties and the hyperfine structure were measured by vibrating sample magnetometry and Mössbauer spectroscopy.

Keywords: Titanomagnetite minerals; Magnetic properties; Microstructure



Introduction

In the coastal section where from originates the magnetite sand for this study exist two units formational: the limestone coralline of the pliocene and the sediments sandy of quaternary. The limestone understand a succession of materials that are a sandy limestone and conglomerate with pebbles of rocks, dense sandy, hard gray limestone, with occasional coral in the part central of the reef, and limestone coralline interstratification with layers of cockle-shell and abundant coral [1]. The sandy sediments of the quaternary that form these beaches are composed by variable proportions of clastic subrounded, fine grain sands (pass the 40 mesh) of very various nature, that can be subdivided in two classes: organic and inorganic. Among the first fragments of coral exist, embryos of mollusks occasional, foraminiferous, algae calcareous. The inorganic part is represented by grains of magnetite, high concentration of pyroxene, quartz, and feldspar in low concentration [1]. The origin of these sands is possible to classify it according to its composition, location and knowledge of the regional geological conditions. Thus, the formation is composed mainly by conglomerates of pieces igneous of various types and probable that as a group they can be an important source of magnetite by the disorder of those components [1].

The titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) are material ferromagnetic and have the spinel structure, but as have electric conductivity appreciable do not possess technical interest, for which the study of the properties detailed of this system has left the investigators of the magnetism of the rocks. Due to the presence of impurities and possible non stoichiometry in the natural samples, the majority of the work has done themselves in synthetic materials [2,3]; although some works exist on titanomagnetite of

volcanic rocks [4,5]. The point of fusion of the series diminishes with the increase of the content of titanium from 1594 °C for $x = 0$ to 1395 °C for $x = 1$ and the oxygen equilibrium pressure in the point of fusion decrease since 1.3×10^{-6} Pa for $x = 0$ to 1.3×10^{-10} Pa for $x = 1$. The addition of Ti^{4+} ion to the magnetite produces a Fe^{2+} ion extra and therefore, the size of the unit cell enlarges with the content of titanium, although not in a lineal way. The distortion of the network of oxygen of the structure, with regard to the cubic pure one, enlarges to the extent that the ions larger of Fe^{2+} enter the tetrahedron places of the structure, and the parameter of oxygen enlarges since the value 0.379 for the pure magnetite to 0.386 for the Ulvöspinel [6].

Cationic distribution

The cationic distribution of the magnetite $Fe^{3+}[Fe^{3+}Fe^{2+}]O_4$ indicates that the high contributions of electrostatic energy and anionic polarization to the total energy of the network are surpassed for the reduction of energy due to the formation of links covalent by the Fe^{3+} in tetrahedral places. The Ulvöspinel has the cationic distribution $Fe^{2+}[Fe^{2+}Ti^{4+}]O_4$, that is favored by the electrostatic energies and of anionic polarization. The Ti^{4+} has a strong preference by the octahedral places of the spinel structure, and only is found in tetrahedral places when there is ions present with a preference by the octahedral places (for example the Ni) [6].

The cationic distribution has been studied for intermediate compositions among the magnetite and the Ulvöspinel, concluding that the tetrahedral places contain so much ions of Fe^{3+} and Fe^{2+} through the majority of the series, by the way, an arrangement among the contributions of the energies [6].

The main purpose in this work is to find information on the magnetic properties from magnetic sands using different techniques.

Experimental

The elementary chemical composition of Fe, Si, Ti, Mn, and Cu of the original sample were determined using an inductively couple plasma (ICP) and optical emission spectrometer. The color and shape of particles in both magnetic and non-magnetic fractions were observed using a stereoscopic optical microscope. The original sample, the magnetic and non-magnetic fractions were observed using a scanning electronic microscope with an energy dispersive spectrometer (EDAX, DX Prime). The crystalline phase presents in the sand were identified by X-rays diffraction. The specific surface area analyzed by the Bet method. The hysteresis loop of the magnetic sand was determined using a vibrating sample magnetometer. The original sample Mössbauer spectrum was measured in constant acceleration using a source of Co⁵⁷ in rodium matrix. The Mössbauer spectra were fitted using a non-linear square minimum method.

Results and discussion

The chemical composition of the magnetic sand have a content of the elements of main interest being the iron and titanium with a 62.46 and 4.48%, respectively. The specific surface area is 1.18m²/g.

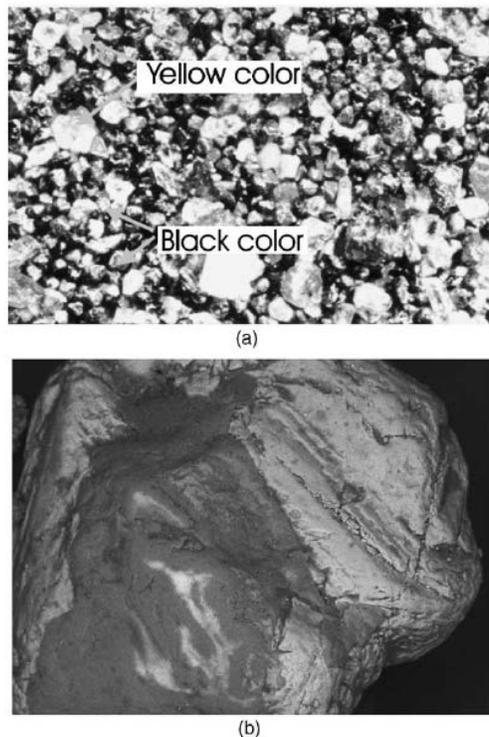


Fig. 1. Photographs of the original sample. (a) Magnetic particles of black color, colorless particles as impurities is of yellow color by stereoscopy microscope; (b) particle covered of a silicate by scanning electronic microscope.

The particles observed in the stereoscopic microscope are of black color in greater proportion and thus also exist as colorless crystalline, yellow, orange, etc. The size particle is found in the average from 75 to 300 μ m (200 to 48 mesh) having a distribution of size in this fraction. As it is observed the morphology that present the particles are of the type subround, large. Fig. 1(a) shows particles of magnetite and hematite of gray and black color, respectively, that are present in greater proportion. Likewise, colorless particles, quartz, silicates as pyrope, garnet and feldspar have been present in small proportion. When the magnetic sand has a mixture of particles of magnetic with silicates is an indication of lack liberation. To know how much is the content of each species a subsequent study of separation is required; concentration of

the minority species is detected using X-ray diffractometer after two mechanical processes.

The magnetic particles with gray and dark colors were analyzed with more detailed in the scanning electronic microscope. Some magnetic particles of the original sample are mixed and possess a different contrast of color, by which, one particle was selected (Fig. 1(b)) that shows in the dark gray section of color to the silicate over the magnetite (clear gray color). To identify this mineral species was carried out a mapping of the elementary composition indicating the minimum quantity of Fe in the area of the center of the particle, also, high concentration of Si was detected, which corresponds to silicate. The distribution of titanium was found in great proportion in the area of the silicate. For the non-magnetic fraction the content of titanium was 15.65% indicating its presence in great quantity and in the magnetic was 5.79%.

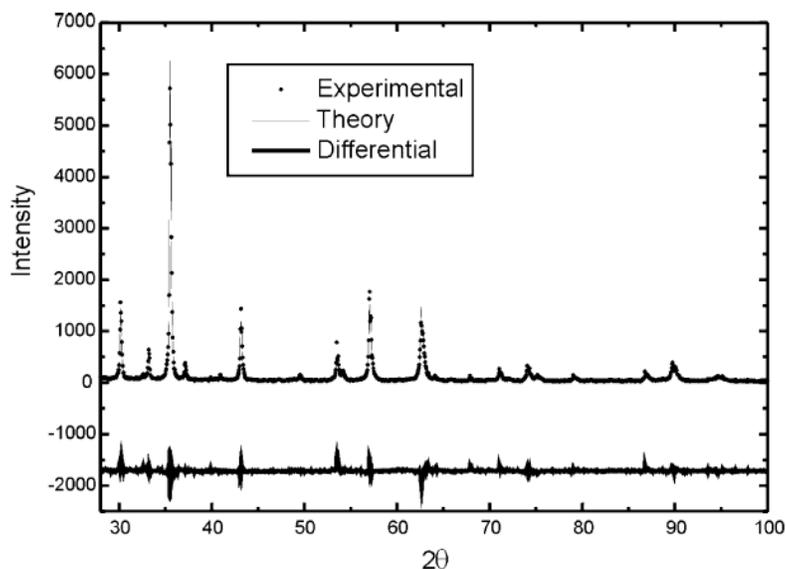


Fig. 2. X-rays diffraction patterns.

The refinement of the X-rays diffraction pattern by the method of Rietveld (Fig. 2) indicates an 86.03% in weight of titanomagnetite and a 13.97% in weight of hematite.

With this refinement the parameter was determined reticular $a = 8.434\text{\AA}$ for the cubic spinel structure of the titanomagnetite. For the structure rhombohedra of the hematite the lattice parameters were estimated as $a = b = 5.062\text{\AA}$ and $c = 13.833\text{\AA}$.

Fig. 3 shows the hysteresis cycle of the magnetic sand with a magnetization of saturation of 55.8 emu/g and a coercivity of 39.6 Oe . Suggesting a process of benefit and a potential use of this mineral that is attainable in three stages. In the first stage, the feasible inverse process of flotation with the objective to remove the impurities. In the second stage, a detailed characterization of the magnetic concentrate was performed in order to quantify the magnetic mixed or freed particles, and quantity of titanium present. The third stage consists of finding a feasible process to elaborate magneto, also other process to concentrate the titanium.

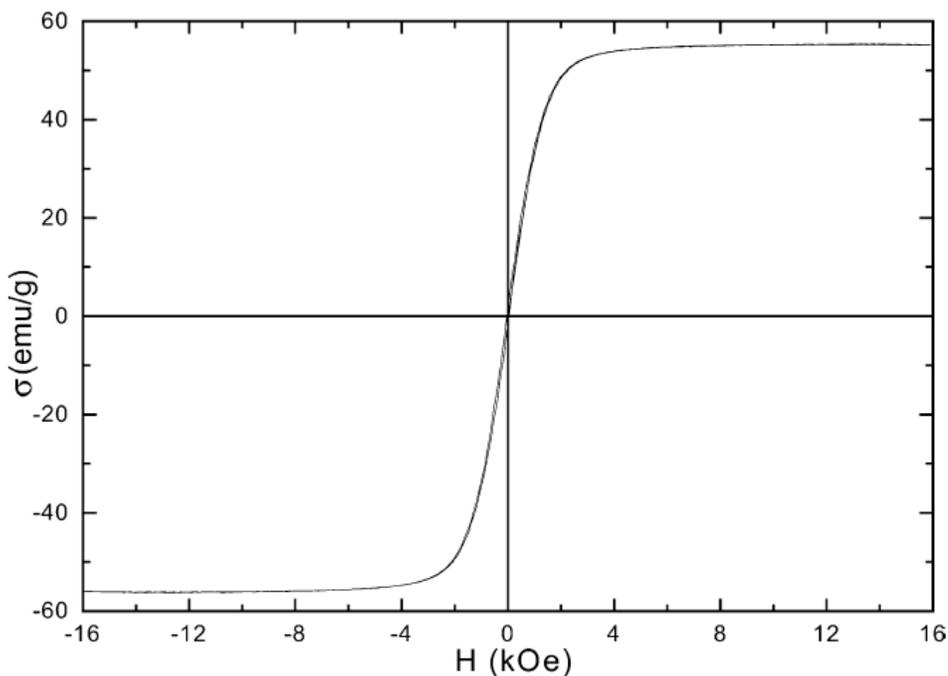


Fig. 3. Hysteresis loop of magnetic sand.

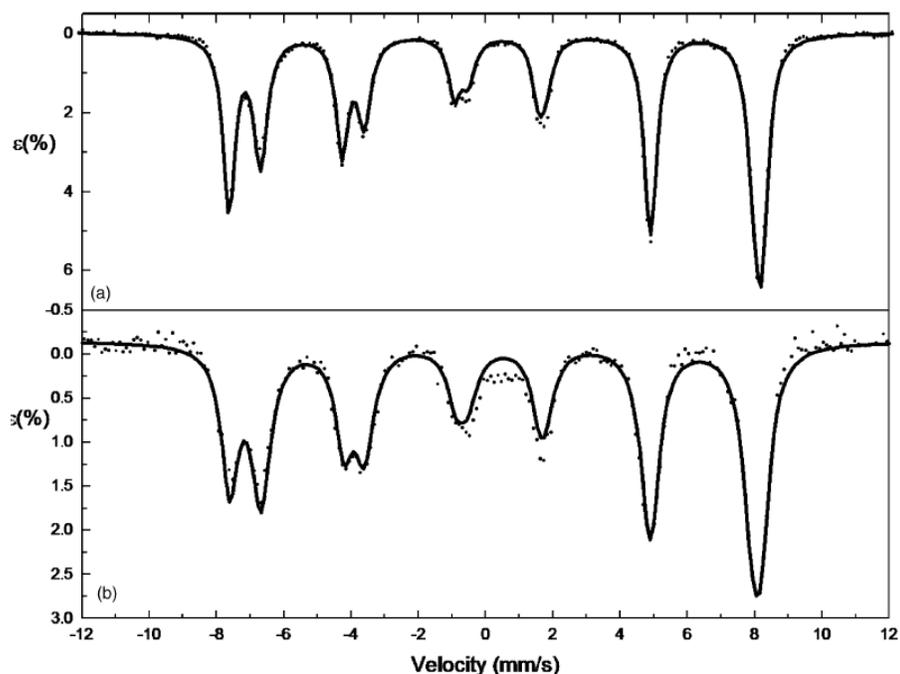


Fig. 4. Mössbauer spectra: (a) magnetite reference sample; (b) original sand sample.

Table 1
Mössbauer hyperfine parameters

Sample	δ (mm/s)		ΔE_Q (mm/s)		H (kOe)	
	Oct.	Tet.	Oct.	Tet.	Oct.	Tet.
Magnetite reference sample	0.306	0.649	-0.011	0.006	492	457
Original sand sample	0.329	0.624	-0.031	0.004	491	454

Fig. 4 shows the Mössbauer spectra of (a) a magnetite reference sample and (b) the original sand sample. Both spectra were fitted using two Zeeman sextets: one for Fe atoms in octahedral sites, the other for Fe atoms in tetrahedral sites. Table 1 shows the hyperfine Mössbauer parameters. The differences are attributed mainly to titanium in magnetite.

Conclusions

The magnetic sand contains mainly titanomagnetite and hematite with impurities as quartz, pyroxene, etc. Approximately 86.03 wt.% titanomagnetite and a 13.97 wt.% hematite were obtained. A lattice parameter $a = 8.434 \text{ \AA}$ was determined for the titanomagnetite with a cubic spinel structure, while for the hematite with structure rhombohedra the lattice parameters were $a = b = 5.062 \text{ \AA}$ and $c = 13.833 \text{ \AA}$. The iron was found mainly in the magnetic component of the particles, while the greater quantity of silicon and titanium is in the non-magnetic component. The particles possess an average size from 75 to 300 μm (200 to 48 mesh) and a specific surface area of $1.18 \text{ m}^2/\text{g}$. The magnetic sand has a magnetization of saturation of 55.8 emu/g and a coercivity of 39.6 Oe. The Mössbauer spectrum is similar to magnetite with differences attributed to the presence of titanium.

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