

MÖSSBAUER SPECTROSCOTIC STUDY OF CHEMICAL STATE OF IRON IN NATURAL SAMPLES HORNBLENDES FROM UDAIPUR DISTRICT (RAJ)

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Abstract— Mössbauer spectroscopy is based on the quantum mechanical “Mössbauer effect,” which provides a non-intuitive link between nuclear and solid-state physics. Mössbauer spectrometry provides unique measurements of electronic, magnetic, and structural properties within materials. Mössbauer study of hornblendes samples are reported here with Mossbauer parameters and also chemical analysis. The state of iron present in the form of Fe^{2+} and Fe^{3+} cations in the samples. The ratio of Fe^{2+} and Fe^{3+} leads to oxidation state of iron oxides which is related to F-factor.

Index Terms— Mössbauer study, hornblendes samples, Oxidation state.

1 INTRODUCTION

MOST applications of Mössbauer spectroscopy in materials science utilize “hyperfine interactions,” in which the electrons around a nucleus perturb the energies of nuclear states. The energy levels of a nucleus are determined mostly by the strong interaction which binds the nucleons together. Mössbauer spectrometry is performed with the nuclei ^{57}Fe . The ^{57}Fe atoms in the lattice oscillate at higher frequencies in at higher temperatures, leading to an energy shift of the accompanying absorption peak from the Doppler Effect. Mössbauer spectroscopy has been widely used to investigate the chemical state of iron in various kinds of hosts in metals [1], [2]. Among the various forms of iron oxides maghemite and hematite are of most importance in technology and industrial applications [3]. Maghemite has numerous application like recording, memory devices, magnetic resonance imaging, drug delivery or cell targeting [4] (Laurent *et al.*, 2008; Daou *et al.*, 2010).

The octahedral coordinated with four oxygen and two hydroxyl ions. Now our aspect has been of major interest. The change in oxidation state with respect to nucleus [5], [6], [7]. The change of spin state with respect to the electronic structure of the iron atom obtained from corresponding Mössbauer experiment [8], [9], [10] and nature of neighbouring atoms and two isomers are distinguished which are either C is form of Trans form [11], [12], [13], [14]. The basic structure feature of

silicate hornblendes is a composite of different site octahedral sites are generally fitted by Mg^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} etc. There are two types of octahedral sites present in silicate depending on the position of the hydroxyl ions. If the hydroxyl ions on the adjacent corner of the site it is known as the C's site. While the corresponding site trans site describe the site situation where hydroxyl ions lie at the opposite corner of the octahedral [15], [16], [18], [19].

The samples were collected of medium grade metamorphism Udaipur district (Raj). Tectonic process, which occur in a higher pressure, high temp environment change the composition and structure of original igneous and sedimentary rocks. Pure fraction of the samples, were obtained from by using gravity magnetic and microscopic separation methods. These samples are ninety-nine percent pure.

2 EXPERIMENTAL METHOD

The hornblendes samples were collected from geology department and Chemical analysis carried out from chemistry department J.N.V University Jodhpur. The Mössbauer spectrometer consist of a electromechanical drive in a constant acceleration mode a proportional counter with accessory electronic backed by a channel analyzer, due to the symmetrical 256 channels and mirror images of each other are recorded simultaneously two typical spectra is displaced in figures 1and 2. The source is mounted on the drive unit which was 10m $CiCo^{57}$ diffuse in to palladium and spectra were recorded in transmission geometry at room temperature the spectra have been analyzed by computer programme. This programme assumes the spectrum to be sum of Lorentzian. We have restricted these fits to maximum of 8 lines corresponding to 4 doubles, ferrous and ferric ions in sites.

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3 RESULT AND DISSCUSSION

3.1 Figures and Table

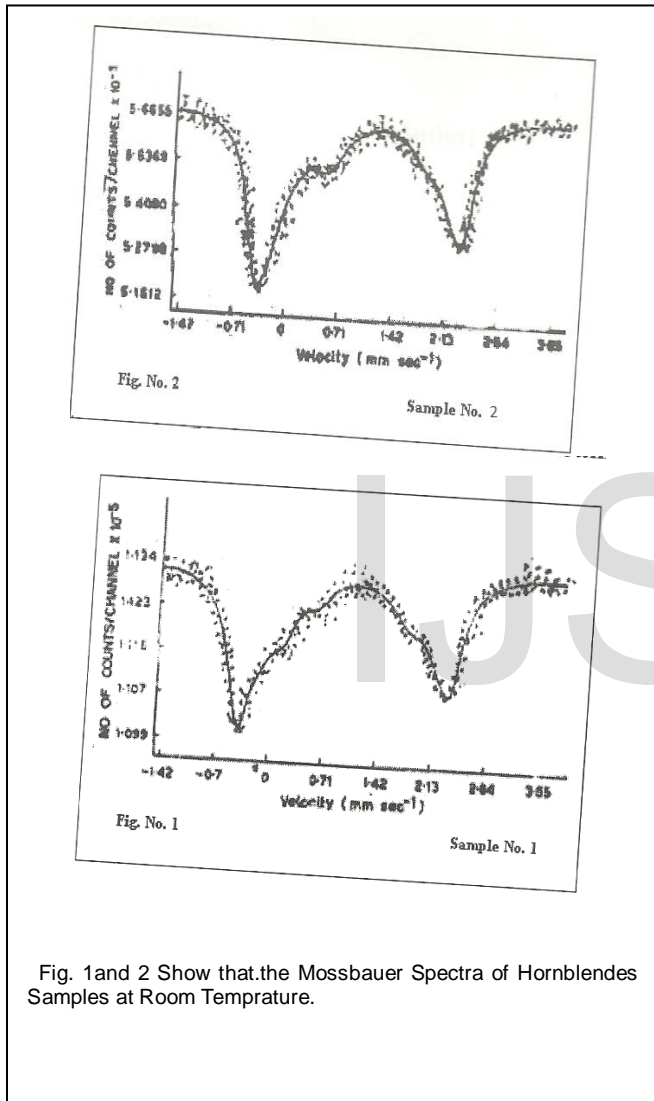


TABLE 1

CHEMICAL ANALYSIS OF SOME HORNBLENDES

Sample	S-1	S-2
SiO ₂	45.44	44.90
TiO ₂	01.48	00.87
Al ₂ O ₃	09.73	12.42
Fe ₂ O ₃	05.84	07.27
FeO	05.88	09.97
MnO	00.12	00.43
MgO	12.50	12.79
CaO	09.49	07.89
Na ₂ O	01.12	01.67
K ₂ O	00.39	00.67
P ₂ O ₅	00.31	00.31

TABLE 2

CHEMICAL COMPOSITION CALCULATION ON THE BASIS OF OXYGEN PER FORMULA

SAMPLE	S-1	S-2
Si	6.7369	6.4467
Ti	0.1637	0.0924
Al ³⁺	0.4372	0.5481
Fe ²⁺	1.2246	1.2051
Fe ³⁺	0.6500	0.7127
Mn ²⁺	0.0142	0.0509
Mg	2.7384	2.8091
Cu ²⁺	1.5131	1.2166
Na ⁺	0.2939	0.4631
K ⁺	0.0712	0.1243

TABLE3

EXPERIMENTAL RESULT OF MOSSBAUER PARAMETERS

SAMPLE	IS	QS	LW	F-FACTOR	ASSIGNMENT
S-1	1.15	2.73	0.32	.50	Fe ²⁺
	1.11	2.33	0.38	.20	Fe ²⁺
	0.88	2.26	0.51	.10	Fe ²⁺
	0.46	0.54	0.53	.20	Fe ³⁺
S-2	1.15	2.83	0.32	.35	Fe ²⁺
	1.16	2.49	0.34	.22	Fe ²⁺
	1.15	1.83	0.53	.19	Fe ²⁺
	0.39	0.72	0.46	.24	Fe ³⁺

Errors in IS ± 0.02% QS ± 0.018% LW ± 0.02%

The Mössbauer lines are fitted in the form of doublets. The isomer shift is varied from 0.39mm/sec to 1.17mm/sec. The isomer are shift depend on electron density at the nucleus. If electron in outermost orbit involves in chemical bonding have a significant perturbing effect on occupied 3s orbital and σ bonds 4s orbital. The isomer shift parameter is sensitive to any

The chemical analysis of samples indicate that the amount of iron oxide is smaller than SiO₂ but Mössbauer spectroscopy can be used to identify iron species because this technique can quantify the proportion of Fe²⁺ and Fe³⁺ in both crystalline and amorphous materials [20], [21]. So iron species is identified as ferric iron of hematite (Fe³⁺), para magnetic ferric iron (Fe³⁺) and para magnetic ferrous iron (Fe²⁺). But Fe²⁺ is the paramagnetic species present in the octahedral sheet of hornblendes. The chemical analysis reveals that the amount of iron is less but which is useful for Mossbauer spectroscopy.

factor that effect the number and distribution of valence shell electron it provide a iron oxidation state, coordination environment and covalent character of bonded anions. Since Fe^{3+} is a low spin cation. So the Fe^{2+} cations no longer retains and electron d^6 orbital of Fe, therefore decrease and electron density at the nucleus produces relatively high isomer shift. The doublet with a smaller quadrupole splitting is ascribed to paramagnetic ferric (Fe^{3+}), presumably originating from clay minerals. The doublet with a larger quadrupole (QS) is attributive paramagnetic ferrous (Fe^{2+}) mostly due to crystalline silicate [22]. When ferrous Fe is bounded to oxygen in silicate, sulphate carbonates increase positive charge of Fe^{3+} ion formed by losing one of its 3d electron and remaining electrons are attracted by nucleus isomer shift ferric mineral are smaller than the ferrous mineral. The covalent bond character is higher tetrahedral coordination than for a cation in an octahedral coordination with O or S. As a result decreased isomer shift correlated with lowering of coordination number of the Fe cation. Non of samples represent the quadrupole splitting zero and Fe nucleus is not spherical in hornblendes. The quadrupole splitting is varied from 0.53mm/sec to 2.84 m/sec. This represent that Fe nucleus are not spherical in the samples, a non spherical component of the electric field. The QS value of Fe^{2+} ion is larger than the QS value of Fe^{3+} ion. This variation indicates that the coordinate sites are destroyed in geometry of hornblendes. Therefore as a result in electronic configuration that is no longer spherically symmetrical and produces an electric field gradient at the nucleus. So QS parameters are significantly higher for Fe^{2+} bearing silicate or oxides than for those minerals containing Fe^{3+} ions. Thus Fe^{2+} and Fe^{3+} ions in hornblendes are to be easily distinguished by Mössbauer spectroscopy. Octahedral coordinated Fe in the majority of rock forming mineral is distinguished from Fe^{2+} ion while Fe^{3+} ions occupy very distorted and noncubic lattice environment around the nucleus. Mössbauer spectroscopy is useful technique for characterizing the valence electronic coordination symmetric and state of occupancies of Fe cations in rock forming minerals. There are two main parameters isomer shift quadrupole splitting and to distinguished Fe^{2+} and Fe^{3+} ions with sites. Peak area is related to recoil free fraction.

4 CONCLUSION

Our main conclusions are as follows.

- 1- The chemical analysis of both samples represent that the amount of iron oxide is very small.
- 2- Both samples are indicating that the iron present in the form of ferrous (Fe^{2+}) and the range of QS is 1.83 to 2.83. it means that ferrous is in low spin state.
- 3- The ratio of Fe^{3+}/Fe^{2+} is more than 50%. This show that Fe^{2+} is in low spin state.
- 4- Mica- Fe is not a reasonable ferric/ ferrous iron standard since it reveals significant variations in degree of oxidation with different size fractions are .1 to .5.

- 5- The QS value of Fe^{2+} is large than the QS values of Fe^{3+} this variation represent that coordinates sites are destroyed in geometry in hornblendes. So Fe^{3+} is not high spin state.

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REFERENCES

- [1] H. Annersten, Amer mineralogist. Mössbauer studies of natural biotites. Vol. 59, pp. 143 (1947).
- [2] M.Blume., Phys. Rev, Letter. Hyperfine Structure and Nuclear Radiation, Vol. 14, pp. 506 (1965).
- [3] Huo L, Li W, Lu L., Cui H., Xi S., Wang J., Zhao B., Shen Y., and Lu Z., Preparation, structure, and properties of three dimensional ordered α - Fe_2O_3 nanoparticulate film. *Chem. Mater.* Vol. 12, No. 3, pp. 790 (2000).
- [4] Daou T. J., Greneche J-M., Lee S-J., Lee S., Lefeverve C., Sylvie B-C., and Pourroy G., Spin canting of maghemite ostudied byu NMR and In-Field Mossbauer spectrometry. *J. Phy. Chem. C* Vol. 114, No. 19, pp. 8794-8799 (2010).
- [5] J. P. Adloff, J. M. Friedt, Pruc, Symp, Mössbauer spectroscopy, apl IAEA. 30 (1972).
- [6] H. H. Wickman, G. K. Wertin, in Chemical application of Mössbauer.
- [7] J. Ensling, B. W Fitzsimmons, P. Gutlich, K.M. Hasselback, *Ang. chem.*, 82 638 (15) (1970).
- [8] J. English, J. Fleisch, P. Gutlich, B. W. Fitzsimmons, *chem. Lett*, 45, 22 (1977).
- [9] R. Chandra, R. P. Tripathi and S.lokanthan, *Phy. Satat*. 88, 633 (1978).
- [10] T. S. Srivastava, A. Nath, *Radiochem radioanal Letters* 16, 103 (1974).
- [11] R. V. Parish, in Ernst A. Koerner von Gustorf , *The organic chemistry of iron*, 2 vols (Academic press, New York, P 175 (1978).
- [12] R. V. Parish, *Prog Inorg chem.*, 15-101, (1972).
- [13] G.K. shenoy and F.E. Wagner, *Mössbauer isomer shifts*, (North Holland, Amsterdam (1978).
- [14] Banchrft G. M Maddock A. G and Burns R. G *Geo Chem, Acta* 31, 2219-2246 (1967).
- [15] Tripathi, R.P. Chandra U. Candra R. And Loknathan S. J. *Inorg, Nucl* (1978).
- [16] Haggstron L. Wappling R. And Annersten H. *Phys. Stat Sol*, 33, 741 (1969).
- [17] Greava C Burns R, G and Barcott, *GM Nature* 61, 229 (1971).
- [18] A.N Nigam, R.P. Tripathi, H.S. Singh and R.S. Gambhir *Indian Journal of pure and applied physics* Vol 25, 188-190, April (1987).
- [19] A.N Nigam, R.P. Tripathi, H.S. Singh and R.S. Gambhir *Fuel (GB)*, 68, 209 (1989).
- [20] A.N Nigam, R.p. Tripathi, H.S. Singh and R.S. Gambhir *Indian Fuel (GB)* 70, 262 (1981).
- [21] J. HILTON, G.J. Long, J.S. CHAPMAN, J.P.LISHMAN, *Geo-chim. Coschin. Acta*, 50, 2147 (1986).
- [22] J.M.D. Coey, D.W. Schindler, F. Weber, *Can.J. Earth Sci*, 11, 1489 (1974).