Mössbauer, X-ray and magnetization studies of basic volcanic and hyperbasal rocks

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The 57Fe Mössbauer, X-ray diffraction and magnetic susceptibility studies were carried on two samples, basic volcanic (basalt) and hyperbasal (dolerite) rocks, collected from Kundal area of Rajasthan, India to identify iron-bearing minerals. Room temperature Mössbauer parameters of basalt sample show the presence of hematite (Fe2O3), aluminium substituted magnesioferrite [Mg(Fe2-xAlx)O4] and illite. Iron is present as both Fe3+ and Fe2+ in illite. Temperature dependence of magnetic susceptibility measurements shows no transition around 120 K (Verway transition) for both the samples, indicating existence of (Mg, Al) substituted spinel ferrites. These results have been corroborated by X-diffraction and chemical analysis of the samples.

[Keyword: Mössbauer parameters, Magnetic susceptibility, Mössbauer spectroscopy, X-ray diffraction]

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1 Introduction

The 57Fe Mössbauer spectroscopy has been widely used to characterize iron bearing minerals present in sedimentary rocks, volcanic ash and coals1-4. Two samples, basic volcanic (basalt) and hyperbasal (dolerite) rocks were collected from Kundal area of Barmer district in western Rajasthan, India. The basic volcanic (basalt) rock occurs as flow whereas hyperbasal (dolerite) as dyke in the area. The Kundal area lies between the Siwana and Jalon ring complexes. These rocks were emplaced at the end of Aravalli Thermal event at about 730±10 Ma as reported by Kochhar5. Chemical compositions of minerals from the volcanic-plutonic rocks of Piplun area of Siwana ring complex have been recently studied by electron microprobe analyser 6. We have thus used Mössbauer spectroscopy, X-ray diffraction and magnetic susceptibility measurements to analyse iron-bearing minerals present in basic volcanic and hyperbasal rocks. The iron bearing minerals present have been characterized through comparison of their Mössbauer parameters with those of mineral samples reported in literature.

2 Experimental Details

Two samples were finely powdered and sieved through 200 μm gauge. The Mössbauer absorbers were the powdered samples mounted in plastic press fit holders. The sample thickness of 50 mg/cm² was used. Thickness of 50 mg/cm² may appear high, but was required in view of the low value of iron content as evidenced from the chemical analysis. Mössbauer spectra were recorded at room temperature using Mössbauer drive in constant acceleration mode coupled with 256-multichannel analyser (Austin Science Inc. USA). A57Co(Rh) source with initial activity of 10 mCi was used and the spectrometer was calibrated regularly using 0.001 inch thick natural iron foil. Mössbauer absorption spectra were computer fitted with Lorentzian line shapes using standard least square minimization technique.

X-ray diffraction patterns of powder rock samples were taken on PW 1140/90 Philips X-ray diffractometer using Cu Kα radiation to identify various minerals present in the samples. Magnetic susceptibility measurements from liquid nitrogen to room temperature were recorded on a Philips Vibration Magnetometer. Chemical analysis of both rock samples was done by wet chemical methods using a Syntronics UV-V15 Mediflame Photometer-127 while Fe2O3 and MgO were determined by Polychromatic in LABTAM-8440, ICP-AES. The results are listed in Table 1.

3 Results and Discussion

3.1 X-ray data

The d-spacing and relative intensities of the prominent lines in the X-ray diffraction patterns of
basic volcanic and hyperbasal rocks shown in Fig. 1 were compared with ASTM data files. The peaks corresponding to (d-spacing in Å ) 2.71, 2.53 and 1.69 have been assigned to hematite\(^7\text{a}\), whereas the peaks at 4.20, 3.31, 2.25 and 2.21 are due to quartz\(^7\text{b}\). The peaks at 2.52, 1.60, 1.48 and 4.49, 3.37, 2.53 indicate the presence of magnesioferrite\(^7\text{c}\) and illite\(^8\), respectively. However, magnetite\(^7\text{d}\) may also exist as its peaks overlap with magnesioferrite. In order to confirm the presence of magnetite or magnesioferrite, magnetic susceptibility measurements were carried out. The non-existence of peaks at 2.77, 2.63 and 1.92 show that calcium aluminoferrite\(^7\text{e}\) is either absent or is below the detectable limit.

### Table 1—Chemical analysis of major constituents (Relative weight percentage) of the rock samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO(_2)</th>
<th>Fe(_2)O(_3)</th>
<th>Al(_2)O(_3)</th>
<th>MgO</th>
<th>CaO</th>
<th>TiO(_2)</th>
<th>Na(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic volcanic</td>
<td>45.51</td>
<td>15.11</td>
<td>14.14</td>
<td>6.13</td>
<td>7.81</td>
<td>2.96</td>
<td>4.01</td>
</tr>
<tr>
<td>Hyperbasal</td>
<td>53.35</td>
<td>12.02</td>
<td>14.98</td>
<td>7.25</td>
<td>4.23</td>
<td>1.09</td>
<td>4.30</td>
</tr>
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</table>

3.2 Susceptibility data

The magnetic susceptibility measurement data of the two rock samples are projected in Fig. 2. There is a smooth decrease in magnetic moment with increase in temperature. No transition around 120 K has been observed. This transition, called Verway transition, is characteristic of the presence of magnetite. Thus, the absence of Verway transition in both the samples confirms non-existence of magnetite. As chemical analysis shows the presence of Mg and Al, therefore, absence of magnetite supports the formation of (Mg, Al) substituted ferrite and is in agreement with X-ray data.

3.3 Mössbauer data

Room temperature Mössbauer absorption spectra of two rock samples are shown in Fig. 3. Hyperfine parameters from the computer fitted spectrum of basic volcanic rock are presented in Table 2. Due to poor resolution and weak absorption in the spectrum for hyperbasal rock (probably due to scarce amount of
iron), computer analysis could not be performed. X-ray diffraction of this sample also corroborates and shows less sharp peaks as compared to basic volcanic rock.

Guided by the shape of the spectrum (basic volcanic rock), the literature and, keeping in view the X-ray studies, the spectrum was fitted with three sextets, and two doublets. Because of overlap in the sextets, one has

Fig. 3—Mössbauer absorption spectra for (a) basic volcanic and (b) hyperbasal rock
to use the constraint of line widths. The crystal structure of hematite is that of corundum ($\alpha$-Al$_2$O$_3$) with close packed oxygen lattice and Fe$^{3+}$ cations in octahedral sites. Magnesio-ferrite (Mg Fe$_2$O$_4$) has a near inverted spinel structure with cations Mg$^{2+}$ and Fe$^{3+}$ unequally distributed among tetrahedral and octahedral sites. In case of presence of Al (as per our chemical analysis), substitution of aluminium goes to the tetrahedral site at the expense of magnesium and iron, thus lowering the value of internal magnetic field.

A perusal of hyperfine parameters, Table 2 and the above stated structure considerations, the outermost sextet is assigned to hematite, whereas the inner sextets are assigned to Fe$^{3+}$ in octahedral and tetrahedral coordination, respectively, in magnesium alumino-ferrite. This conjecture is strengthened as our chemical analysis also shows the presence of magnesium and aluminium in sufficient amount, required for formation of magnesium-alumino-ferrite. Hyperfine fields, for magnesium-alumino-ferrite in our sample, are in between those reported for pure MgFe$_2$O$_4$ ($H_{\text{oct}}= 496$ kOe, $H_{\text{tet}}= 464$ kOe) and for magnesioaluminoferrite Mg$_2$Al$_2$O$_5$ ($H_{\text{oct}}= 460$ kOe, $H_{\text{tet}}= 427$ kOe) suggesting small substitution of Al in the sample.

Small observed value of magnetic field in hematite also supports the low substitution of aluminium. The paramagnetic components observed in the spectrum are assigned to Fe$^{2+}$ and Fe$^{3+}$ illite as the Mössbauer parameters obtained from these two doublets are very close to the reported values quoted for these two phases.

Thus the Mössbauer results are in agreement with X-ray diffraction and magnetic susceptibility measurements. Furthermore, our magnetic susceptibility and Mössbauer measurements could differentiate between magnesioaluminoferrite and magnetite.

**Acknowledgements**

The authors are thankful to Dr. A. Krishnakanta Singh, Department of Geo-Physics, Kurukshetra University, Kurukshetra for chemical analysis of the samples.

**References**

7. X-ray diffraction (ASTM data) file No. (a) 13-534 (b) 5-490 (c) 11-9 (d) 19-629 (e) 11-124.

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**Table 2**—Hyperfine interaction parameters for basic volcanic rock (basalt) from Rajasthan, India computed from Mössbauer spectrum recorded at room temperature, Isomer shift ‘$\delta$’ is given relative to $\alpha$-Fe,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Site</th>
<th>$H$</th>
<th>$\delta$(Fe)</th>
<th>$\Delta$</th>
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</thead>
<tbody>
<tr>
<td>Basic volcanic rock</td>
<td>Hematite ($\alpha$-Fe$_2$O$_3$)</td>
<td>$M_1$ (Octahedral) $M_2$ (Octahedral)</td>
<td>509</td>
<td>0.37</td>
<td>-0.20</td>
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<td></td>
<td>Mg(Fe$_{2-x}$Al$_x$)O$_4$ Illite Fe$^{3+}$</td>
<td>$M_3$ (Tetrahedral)</td>
<td>486</td>
<td>0.70</td>
<td>-0.0</td>
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<td>Fe$^{2+}$ Illite Fe$^{3+}$</td>
<td>$D_1$</td>
<td>466</td>
<td>0.39</td>
<td>-0.0</td>
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<tr>
<td></td>
<td></td>
<td>$D_2$</td>
<td>-</td>
<td>0.31</td>
<td>0.65</td>
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<tr>
<th>Sample</th>
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<th>Site</th>
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<th>$\delta$(Fe)</th>
<th>$\Delta$</th>
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<tr>
<td>Literature Values</td>
<td>Hematite ($\alpha$-Fe$_2$O$_3$)</td>
<td>(Octahedral)</td>
<td>517</td>
<td>0.38</td>
<td>-0.21</td>
</tr>
<tr>
<td></td>
<td>Mg(Fe$_{2-x}$Al$_x$)O$_4$ Illite (Octahedral)</td>
<td>(Tetrahedral)</td>
<td>490-495</td>
<td>0.35</td>
<td>-0.0</td>
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<tr>
<td></td>
<td>Fe$^{2+}$ Illite Fe$^{3+}$</td>
<td>$D_1$</td>
<td>460-469</td>
<td>0.38</td>
<td>-0.0</td>
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<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
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<th>$H$</th>
<th>$\delta$(Fe)</th>
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<tbody>
<tr>
<td></td>
<td>Fe$^{2+}$ Illite Fe$^{3+}$</td>
<td></td>
<td>-</td>
<td>1.01-1.35</td>
<td>2.50-2.70</td>
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<tr>
<td></td>
<td></td>
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<td>-</td>
<td>0.30-0.50</td>
<td>0.60-0.90</td>
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