Dehydroxylation of Minerals of Gadisunkapur Area with Special Reference to FTIR and Thermal Study

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Abstract: This paper attempts to explain the presence of OH group for micas along with some sulfate, chloride, quartz and feldspar minerals. These minerals are found to be associated with barite vein, metasediments (quartz-chlorite schist), metarhyolite and varieties of granitic rocks of Gadisunkapur area of Hungund-Kushtagi Schist belt. The samples were collected in and around Gadisunkapur village of Bagalkote district, Karnataka and further processed to determine OH group anion in different minerals present based on FTIR and Thermal studies such as Thermogravimetric analysis (TGA) and Differential Thermal analysis (DTA). The high temperature dehydroxylation is investigated using this analysis. Furthermore, present study indicates the presence of different extra species (CO2, CO3,2- and OH). The results show the incorporation of CO2 into the structures due to heating or enhanced by the dehydroxylation process.

Keywords: FTIR, TGA, DTA, OH group, Gadisunkapur, Hungund-Kushtagi schist belt.

Introduction

Gadisunkapur area has some barite traces, barite occurrence in the study area rocks are having mica, feldspar, chlorite and quartz minerals. Biotite and muscovite are the dominant phyllosilicates observed in the lithounits of the study area. Fourier Transform Infrared Spectroscopy (FTIR) and Thermal study carried out in the study area shows the presence of OH molecules. The shape of micas is primarily based on interconnected six member rings of SiO4 tetrahedra that make bigger in endless sheets. Three out of 4 oxygen’s from each tetrahedron are shared with different tetrahedra. This ends in a simple structural unit of Si2O7. FTIR and thermal studies play a prominent role in identifying the minerals present in the rock samples of the study area. In geology, natural micas release cation when subjected to weathering and hydrothermal alterations (Kapoor et al., 1981; Taylor et al., 2000). The thermal study and FTIR carried out gives the detailed spectral changes related to different vibrational bands (e.g. these of O-H, Si-O, Al-O vibrations) and is compared with IR data.

Geological setting

The Hungund-Kushtagi schist belt is having a general trend of NW-SE that is exposed inside the northwestern part of Eastern Dharwar Craton (EDC). Geologically, the belt mainly includes mafic volcanic rocks with subordinate felsic volcanic rocks and metasediments (quartz-chlorite schist, banded iron formation, meta argillite and greywacke) Bhat et al (1996). According to Naqvi et al., (2006) said geochemically volcanic rocks are high Mg, high Fe, and excessive Mg-Fe basalts, high Mg-dacites, andesites and adakites. A form of granitoids is exposed inside the adjoining place of the greenstone belt (Dey et al. 2003, 2009, 2012; Dey, 2006, 2011; Mohan et al, 2013).

Rocks of Hungund-Kushtagi schist belt are divided into Ilkal and Muddenur formations. The study area falls in contact zone of Ilkal and Muddenur formations and composed of amphibolites, metabasalts, metasediments (quartz, chlorite-schist), metarhyolite and varieties of granites. In the study area few barite veins are also reported which are associated with metabasalts, metasediments and granites. The amphibolite of the study area occurs as lensoid bodies which are reported in the northeastern area of Gadisunkapur village adjacent to Ilkal halla. The granites pink and grey variants are seen in western part of Gadisunkapur village, along Raichur-Bachi state highway. These granites show porphyritic texture. Barite occurs in vein forms varying from 2-4meter in width and 10-20meters length within metasediments (quartz-chlorite- schist) and rarely traces are found in granites. Metarhyolite is observed in the western and north eastern part of Jammaldinni village which shows aphanitic texture with varying colour from light green to reddish brown (Maruulradhya et al, 2019).

Materials and Methods

Fourier transform infrared (FTIR) spectroscopy is an alternative technique for acquiring quantitative mineralogy. The mineralogy of a combination may be extracted from its FTIR spectrum because minerals show most of the fundamental vibration modes in the mid-infrared region 4000cm-1 to 400cm-1. Infrared spectra of minerals of Gadisunkapur area were carried out using Carl Zeiss UR-10 and X-99 IR spectrometer.
with the help of mull media method. The collected samples were finely powdered into 150# size then small quantity of powdered samples was taken in agate mortar and powdered to attain size of talcum powder. This powder is mixed with pure paraffin oil forming a suspension of minute crystallites in a viscous medium. Furthermore, skinny plate is prepared through squeezing and (of both Nacl or KBr) plate of resultant received paste (Mahesh et al., 2014).

Fig. 1 Geological map of the study area

Thermogravimetric evaluation is a way in which weight reduction of substance is studied while it is subjected to controlled temperature. TGA approach performs an essential function in finding distinct minerals in geology. Many times TGA curve resembles to the DTA curve of the mineral. When powdered sample is subjected to heating up to the temperature 1400°C, it loses its weight for a period of 15minutes. A 0.5gm of powder has been taken and the weight reduction of substance is calculated and plotted in graph (Rajendra et al., 2018).

Differential thermal evaluation (DTA) is a method wherein the temperature distinction between a substance and a reference material is measured as a characteristic of temperature, while the substance and reference materials are subjected to the same controlled temperature. DTA requires reference fabric, which is referred to as substance. It is usually thermally inactive over the temperature variety. The crucial character of the reference material is its thermal traits and the particle length. DTA method could be very beneficial in identifying minerals, which goes through transformation which is heated to controlled temperature beneath 1400°C (Rajendra et al., 2018).

DTA technique is useful in both qualitative and semi-qualitative studies, which liberates or absorbs energy when subjected to heating and results in transformations such as dehydration, oxidation, decomposition, phase changes and dehydroxylation (Rajendra et al., 2018).

Results and Discussion

The bands between the range 3400cm⁻¹ to 3700cm⁻¹ with stretching vibration of V(OH) indicate the presence of OH molecule for chlorite mineral. The OH deformation of water for specific clay minerals is determined in the range of 1612cm⁻¹ to 2336cm⁻¹ (Saikia et al., 2010). The peaks at 3782cm⁻¹ and 3684cm⁻¹ are assigned V(OH) vibration of OH molecule which suggests the presence of biotite. A stretching vibration for biotite of adsorbed water V(H₂O) is found at 3374cm⁻¹. Further the study band around 1595cm⁻¹ shows the presence of adsorbed water of OH for biotite. The untreated sample did not incorporate CO₂⁻ and CO₃⁻ species due to lack of their characteristic absorption indicators at 1400cm⁻¹ and close to 2345cm⁻¹. The structurally incorporated hydroxyl groups in mica show O-H stretching bands around 3626cm⁻¹, 3702cm⁻¹ and 3590cm⁻¹ (Ming Zhang et al., 2005). The bands around 3414cm⁻¹ show V(H₂O) (Adsorbed water) for micas. Furthermore, the strong bands around 1595cm⁻¹ are assigned to δ(H₂O)/(adsorbed water) which suggest the presence of mica.

The differential thermal analysis noted from 932° to 1169° C shows dehydroxylation of biotite, which is endothermic in nature where water loss is observed as a result of internal arrangement of the atoms.

Weight loss of 0.084% to 0.936 from the temperature 168.61°C to 394.67°C is attributed to dehydroxylation of muscovite. During the dehydroxylation of muscovite, structural transformation of layer silicates were reported (Muller et al., 2000). In muscovite, the O-H vector does no longer point directly in the direction of the interlayer cation, instead the proton is close to the interlayer cation, K, and a bonded oxygen [K-O(2)] of the basal oxygen-atoms plane. The K-O(2) bond distance is longest at room temperature and therefore is considered as weakest (Guggenheim et al., 1987). At high temperatures studied, this bond remains longer and increases in length at rapid rate than the other K-O bonds. The closeness of the proton to the K-O(2) bond and the rate at which this bond weakens at high temperatures suggests the way for dehydroxylation (Annibale et al., 2002). Weight loss of 0.050% to 0.423% from the temperature 432.02°C to 688.66°C is attributed to dehydroxylation of quartz admixture of magnetite, olivine and spinel. The total mass loss of the sample is due to liberation of adsorbed water and hydroxyl group from the lattice structure which corresponds to the formation of new phases like α-β quartz inversion at temperature around 500°C and Si-Al spinel formation at temperature 650°C (Escalera et al, 2012). Weight loss of 0.275% to 3.33% from the temperature 1027.13°C to 1169.09°C is attributed to dehydroxylation of cristoballite leading to formation of mullite which depends on potassium and iron contents in the samples (Fig. 5.9-5.16).
Table 1: Bands in the infrared spectrum of minerals

| S.No | Sample No | Frequency in Cm⁻¹ | Tentative assignment | Mineral identified |
|------|-----------|-------------------|----------------------|-------------------|
| 1    | S-4       | 3702.70w          | V(OH)                | Chlorite          |
|      |           | 3414.05b          | (Adsorbed water)     | Biotite           |
|      |           | 1595.09s          | δ(H₂O) (adsorbed water) | Biotite         |
| 2    | S-7       | 3735.08w          | V(OH)                | Biotite           |
|      |           | 3702.70w          | V(OH)                | Chlorite          |
|      |           | 3626.17sh         | V(OH)                | Chlorite          |
|      |           | 3590.84sh         | V(OH)                | Biotite           |
|      |           | 3413.15b          | V(H₂O) (Adsorbed water) | Biotite        |
|      |           | 1595.09s          | δ(H₂O) (adsorbed water) | Biotite         |
| 3    | S-10      | 3732.13w          | V(OH)                | Biotite           |
|      |           | 3702.70w          | V(OH)                | Chlorite          |
|      |           | 3629.11w          | V(OH)                | Chlorite          |
|      |           | 3415.35b          | V(H₂O) (Adsorbed water) | Biotite        |
| 4    | S-11      | 3767.46w          | V(OH)                | Biotite           |
|      |           | 3649.71w          | V(OH)                | Muscovite         |
|      |           | 3614.39sh         | V(OH)                | Muscovite         |
|      |           | 3418.61b          | V(H₂O)               | Muscovite         |
| 5    | S-17      | 3732.13w          | V(OH)                | Biotite           |
|      |           | 3696.81w          | V(OH)                | Biotite           |
|      |           | 3375.78b          | V(H₂O) (Adsorbed water) | Biotite        |
| 6    | S-19      | 3735.08w          | V(OH)                | Biotite           |
|      |           | 3619.21w          | V(OH)                | Muscovite         |
|      |           | 3402.45b          | V(H₂O) (adsorbed water) | Biotite        |
| 7    | S-21      | 3732.13w          | V(OH)                | Biotite           |
|      |           | 3699.75w          | V(OH)                | Biotite           |
|      |           | 3624.35s          | V(OH)                | Muscovite         |
|      |           | 3373.86b          | V(H₂O) (adsorbed water) | Biotite        |

Fig. 1 Infrared spectra of sample

Table 2: Results of differential analysis of (DTA) of barite of Gadisunkapur area (after Marularadhya and Sreenivasal, 2019)

| S.No | Sample name | Endothermic peak | Mineral identified | Type of Reaction |
|------|-------------|------------------|--------------------|------------------|
| 1    | S-4         | 1162.22° - 1167.72°C | Biotite            | Dehydroxylation  |
| 2    | S-7         | 1163.47° - 1169.90°C | Biotite            | Dehydroxylation  |
| 3    | S-10        | 1162.25° - 1167.29°C | Biotite            | Dehydroxylation  |
| 4    | S-11        | 1151.64° - 1157.55°C | Biotite            | Dehydroxylation  |
| 5    | S-17        | 1101.11° - 1141.44°C | Biotite            | Dehydroxylation  |
| 6    | S-19        | 1107.36° - 1129.61°C | Biotite            | Dehydroxylation  |
| 7    | S-21        | 932.07° - 1008.02°C  | Biotite            | Dehydroxylation  |
| 8    | S-23        | 1084.70° - 1147.00°C | Biotite            | Dehydroxylation  |

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Table 3 Results of thermo-gravimetric- analysis (TGA) of barite of Gadisunkapur area (after Marularadhya, and Sreenivasa, 2019)

| S.No | Sample | Weight loss % | Temperature       | Mineral Identified       | Type of reaction          |
|------|--------|---------------|-------------------|--------------------------|---------------------------|
| 1    | S-4    | 0.1575        | 203.95°-246.11°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.2377        | 362.48°-363.51°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.2577        | 381.81°-382.51°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.1468        | 433.42°-434.49°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 0.1897        | 623.04°-682.92°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 2.314         | 1066.84°-1145.71°C| Cristobalite             | Dehydroxylation           |
| 2    | S-7    | 0.2530        | 168.61°-278.49°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.1286        | 432.02°-433.06°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 0.0988        | 490.05°-490.34°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 0.1984        | 624.75°-625.93°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 0.0501        | 686.17°-688.66°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 1.964         | 1027.13°-1127.63°C| Cristobalite             | Dehydroxylation           |
| 3    | S-10   | 0.333         | 201.67°-243.42°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.225         | 384.70°-385.25°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.081         | 456.49°-457.23°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 0.153         | 604.58°-663.22°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 1.863         | 1037.35°-1131.07°C| Cristobalite             | Dehydroxylation           |
| 4    | S-11   | 0.554         | 393.70°-394.67°C  | Muscovite                | Dehydroxylation           |
|      |        | 3.338         | 1144.65°-1169.09°C| Cristobalite             | Dehydroxylation           |
| 5    | S-17   | 0.481         | 201.65°-271.21°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.260         | 330.04°-369.56°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.376         | 572.59°-668.77°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 0.653         | 1097.80°-1098.84°C| Cristobalite             | Dehydroxylation           |
| 6    | S-19   | 0.103         | 201.79°-255.28°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.084         | 342.07°-374.05°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.423         | 535.92°-687.13°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
| 7    | S-21   | 0.275         | 1131.54°-1163.87°C| Cristobalite             | Dehydroxylation           |
|      |        | 0.936         | 214.49°-308.23°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 0.369         | 588.64°-643.18°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |
|      |        | 0.368         | 865.81°-901.53°C  | Cristobalite             | Dehydroxylation           |
|      |        | 0.528         | 1029.90°-1103.74°C| Cristobalite             | Dehydroxylation           |
| 8    | S-23   | 0.264         | 198.11°-251.37°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.147         | 336.01°-372.75°C  | Muscovite                | Dehydroxylation           |
|      |        | 0.288         | 533.20°-651.13°C  | Quartz admixture of magnetite, olivine and spinel | Dehydroxylation |

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