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Assessment of carbonate concentration and characterization of marine sediments by Fourier Transform Infrared Spectroscopy

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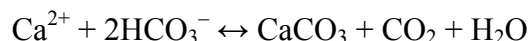
Abstract

Fourier Transform Infrared Spectroscopy (FTIR) is a well established method for the characterization of mineralogical and geochemical properties of marine sediments. Understanding the biogeochemical changes in marine ecosystems is challenging task since it requires adequate analytical techniques and efforts. Biogeochemical characteristics of twenty one marine sediment samples collected off Chennai coast, Bay of Bengal, India were analyzed using FTIR spectroscopy. The FTIR peaks at 1460 cm^{-1} (stretching vibration) and 880 cm^{-1} (bending vibration) were used for carbonate determination. To verify the FTIR results, the obtained carbonate data were compared with carbonate values obtained by chemical analyses. The ranges of carbonate in sediments using FTIR and chemical analyses were 4.5–9.6% and 4.8–10%, respectively. The significant positive relationship was obtained between the carbonate results of FTIR and chemical analyses. This study demonstrates that instead of expensive and time consuming chemical methods, FTIR spectroscopic technique is found as a suitable, rapid and effective method for the quantification of carbonate in marine sediments.

Keywords: FTIR spectroscopy, Carbonate, Biogeochemistry, Chemical analysis, Marine sediments

1. Introduction

Calcium carbonate is a chemical compound with the formula of CaCO_3 . It is a common substance found in rocks in all parts of the world, and is the main component of shells of marine organisms, snails, pearls, and eggshells. Calcium carbonate is produced by marine organisms in the form of two main polymorphs, calcite and aragonite. Its solubility increases with pressure and decreases with temperature. Aragonite is the more soluble phase; hence its saturation horizon is shallower than that calcite [1]. Elements such as Ca^{2+} and Mg^{2+} , in addition to their substantial contribution to marine sediments, are used biologically in vital cellular processes and in the mineralization of skeletons and shells, made of calcium carbonate [2]. Carbonates form from the local saturation of alkaline earth metal ions (Ca^{2+} and Mg^{2+}) in combination with bicarbonate (HCO_3^-) and are summarized here [3]:



Oceanic production of CaCO_3 is usually attributed to the shells of marine planktonic organisms, specially coccolithophores, foraminifera and pteropods. Biogenic carbonates are formed in surface waters and within surficial sediments, and eventually accumulate at the seafloor [4].

The current rate of anthropogenic CO_2 release leads to a surface ocean environment characterized not only by elevated dissolved CO_2 and decreased pH [5] but critically, decreased saturation with respect to calcium carbonate (CaCO_3), a compound widely used by marine organisms for the construction of their shells and skeletons. Because direct ocean geochemical proxy observations are still relatively scarce, past ocean acidification is often inferred from a decrease in the accumulation and preservation of CaCO_3 in marine sediments, potentially indicated by an increased degree of fragmentation of foraminiferal shells. The geological record is imprinted with numerous examples of biotic responses to natural perturbations in global carbon cycling and climate change, some of which could have been caused by large-scale ocean acidification. By reconstructing past changes in marine environmental conditions, Honisch et al.[6] have tested hypotheses for the causes and effects of further relevant stressors such as ocean acidification on ecosystems. Thus, a rapid, cheap and non-destructive tool is required to investigate the distribution of CaCO_3 in sediments for the understanding of the fate of biologically produced carbonate.

FTIR spectroscopy is one of the classical methods for molecular characterization of organic and inorganic species. This standing is due to its sensitivity to the chemical composition and architecture of molecules. The basic principle of the FTIR spectroscopic technique is that those vibrations of covalent chemical bonds that cause a change in dipole moment absorb infrared energy at specific wavelengths. The spectral locations of infrared absorption are indicative of specific chemical bonds or functional groups. Absorption intensity can be measured by either reflectance or transmittance over a wide range of wavelengths, and with Fourier transform instruments, measurements with sufficient signal to noise ratio take on the order of minutes [7, 8]. FTIR spectroscopy has certain advantages over the other techniques, such as the small quantity of sample is required, quick and easy sample preparation and short time to analysis. It also allows the simultaneous study of organic and inorganic species, crystalline or amorphous compounds [9-11] and in some cases, it even provides mineralogical information [12]. Vagenas et al [13], Mecozzi et al [14], and Tatzber et al [15] used FTIR spectroscopy to determine carbonate content in CaCO_3 polymorphs, marine sediments and soils, respectively. Many publications have already dealt with carbonate spectra obtained from infrared spectroscopy, and a detailed description of the underlying functional groups of the respective peaks found their studies [7, 8, 13-16]. Therefore, it seems useful to search for a way to quantify the carbonate content in marine sediments with infrared spectroscopy.

The aims of present work were (1) to investigate the mineralogy and geochemistry of marine sediments off Chennai, using FTIR spectroscopy and (2) to find a rapid and cheap tool for the quantification of carbonates in order to understand the present and past impacts of ocean acidification on marine sediments.

2. Materials and methods

2.1. Sampling

Twenty one surface sediment samples were collected off Chennai coast, Bay of Bengal, India, in 6th April 2009 by a fishing boat using a Van Veen grab sampler (Figure 1). Positions of the sampling locations were identified using a hand-held Garmin Global Positioning System (GPS). The water depth at each sampling point was determined using Single-beam echo-sounder. Samples were taken from the central part of the grab sampler to avoid any metallic contamination from the metallic sampler. The

collected sediment samples were stored in labeled self seal plastic bags and were frozen at -4°C immediately onboard until further analysis.

2.2. FTIR analysis

Sediment samples were prepared for analysis by sieved to 2 mm, ground with an agate mortar, dried for 24 h at 105°C . 2 mg of sediment sample was mixed with a swinging mill with about 200 mg KBr and this mixture was pressed to obtain a transparent pellet. The pellet was dried in desiccators ($> 6\text{h}$) before analysis. FTIR spectra of sediment samples were recorded in the spectral range of $4000\text{--}400\text{ cm}^{-1}$ using Perkin–Elmer Spectrum RxI spectroscopy equipped with a mullard I-alanine doped deuterated triglycine sulphate (DTGS) detector. Prior to the analysis, the waveguide chamber was purged with dry air for 5 min to minimize the water vapor interferences. The recording was performed with a resolution of 4 cm^{-1} and 16 scans per sample. Each spectrum was corrected against pure KBr and the ambient air as a background spectrum. According to Beer- Lambert's law, the magnitude of a signal is proportional to the concentration of the respective component causing IR absorption at its specific wavelength, allowing quantitative conclusions. For this reason, instead of transmission spectra, we used absorption spectra for analysis. Omnic software was used on the spectral data for baseline correction and for conversion from transmittance (T) to absorption (A), according to the equation: $A = \log (1/T)$. The calibration of the FTIR measurements was performed with pure CaCO_3 in KBr.

2.3. Chemical analysis

The percentage of calcium carbonate in the bulk sediment sample was determined on the basis of total inorganic carbon (TIC), which is obtained from total carbon (TC) and total organic carbon (TOC) measurements. TC and TOC of sediment samples were determined with a CHNS elemental analyzer (Perkin Elmer Series II Model 2400 CHNS/O analyzer). Samples for TOC measurements were treated with ethanol and HCl and then heated for two hours at 250°C to remove TIC. A salt correction was applied to TC and TOC raw data; hence CaCO_3 contents are reported per mass of salt-free dry sediment.

3. Results and discussion

3.1. Characterization of sediments by FTIR

The representative FTIR spectrum of Chennai coastal sediment is shown in Figure 2. Briefly, spectrum showed peaks associated with quartz, feldspar, clay minerals, organic matter and carbonate.

Low intensity peaks between 3700 and 3600 cm^{-1} corresponding to oxygen – hydrogen bonds, which indicate the presence of clay minerals [17]. The additional bands at 3699 and 3620 cm^{-1} are due to the presence of kaolinite [18]. The broad band is located at 3430 cm^{-1} could be attributed to the OH stretching of the H_2O molecule, which might also belong to the organic fraction of sediments. The peaks from 2900 to 3000 cm^{-1} are corresponding to C–H stretching vibrations of aliphatic hydrocarbons [19], whereas the peaks from 1620 to 1630 cm^{-1} are caused by stretching vibrations of C=O (Carboxylate groups) organic matter [20–22]. The peaks from 900 to 1100 cm^{-1} could be the characteristic bending of Al-OH and stretching of Si-O vibrations of weathered sheet silicates, principally illite and kaolinite [22]. The peaks at 1088, 797, 778, 693, 470 cm^{-1} could be the presence of quartz mineral [23]. The peak at 1460 cm^{-1} could be stretching vibration of carbonate, whereas 880 cm^{-1} bending vibrations of carbonate [24]. The obtained spectra in this study compare favorably with those reported in the literature on marine sediments [19, 25–28].

3.2. Infrared spectra of pure CaCO_3 and bulk sediment samples

The typical FTIR spectrum of pure CaCO_3 is shown in Figure 3. Calcium carbonate (calcite) has three characteristic IR absorption peaks in the range between 400 and 4000 cm^{-1} : ν_3 at 1460 cm^{-1} , ν_2 at 880 cm^{-1} , and ν_4 at 712 cm^{-1} . Tatzber et al [15] also produced very similar results on pure calcite, using a different instrument (Perkin Elmer Paragon 500 spectrometer). All of these absorptions are influenced by the different ways in which the C–O bonds of the carbonate unit interact with the infrared radiation [26]. Calcium carbonate has three crystalline structures named as the minerals, calcite, aragonite and vaterite and they all have the same chemical composition. Each crystalline form has a different infrared spectrum. In calcite the ion CO_3^{2-} shows D_{3h} symmetry and in aragonite C_s . The symmetry for vaterite is unknown [23].

To verify the carbonate band assignments, spectra of HCl treated sediments were recorded. Figure 4 showed the spectra of untreated and HCl treated sediments. The significant information from this comparison was the disappearance of the peaks at 1460 and 880 cm^{-1} . The disappearance of these peaks in the FTIR spectrum of HCl treated sediment confirmed that these peaks belong to the carbonate ion. Thus, the intensities of bands at 1460 and 880 cm^{-1} were considered for carbonate measurements using peak area method. For the peak area method, the areas were calculated after drawing the baseline between the nearest valleys of the peak between 1360 and 1580 cm^{-1} , and also between 835 and 905 cm^{-1} .

¹.The aforementioned peak areas addressed to carbonate were quantified and averaged. The carbonate content results obtained by FTIR spectroscopy in sediments samples ranged from 4.5 to 9.6%, whereas carbonates by chemical analysis ranged from 4.8 to 10%. Both the methods gave similar results, however, results obtained from FTIR spectra depend on the spectral band (1460 and 880 cm^{-1}) used for the carbonate determination.

The quantified carbonate results from FTIR spectroscopy are compared to results obtained by chemical analysis (Figure 5). The comparative analysis revealed that the calibration and validation correlation coefficient ($R^2 = 0.957$, $p < 0.05$) is satisfactory. To map the geological long-term record for a variety of global environmental perturbations, including ocean acidification plus their associated biotic responses using chemical analyses would be impractical in terms of time and cost per analysis. Thus, this study proves that FTIR spectroscopic technique is found to be a suitable, cheap and rapid method for detailed study of carbonate contents in marine sediments.

Conclusion

In this study, an attempt has been made to quantify the carbonate content using FTIR spectroscopy in marine sediments off Chennai, Bay of Bengal, India. FTIR spectra for all sediment samples showed peaks associated with quartz, feldspar, clay minerals, organic matter and carbonate. Carbonate contents in marine sediments are quantified from FTIR spectra band areas of 1460 and 880 cm^{-1} . CaCO_3 values in marine sediments are also quantified using chemical analysis. The ranges of carbonate in sediments using FTIR and chemical analysis are 4.5–9.6% and 4.8–10% respectively. The significant positive relationship has been observed between the results obtained by FTIR method and chemical analysis. Thus, Fourier Transform Infrared Spectroscopy is found to be a rapid, cheap and promising technique for identifying and quantifying carbonate mineral in marine sediments.

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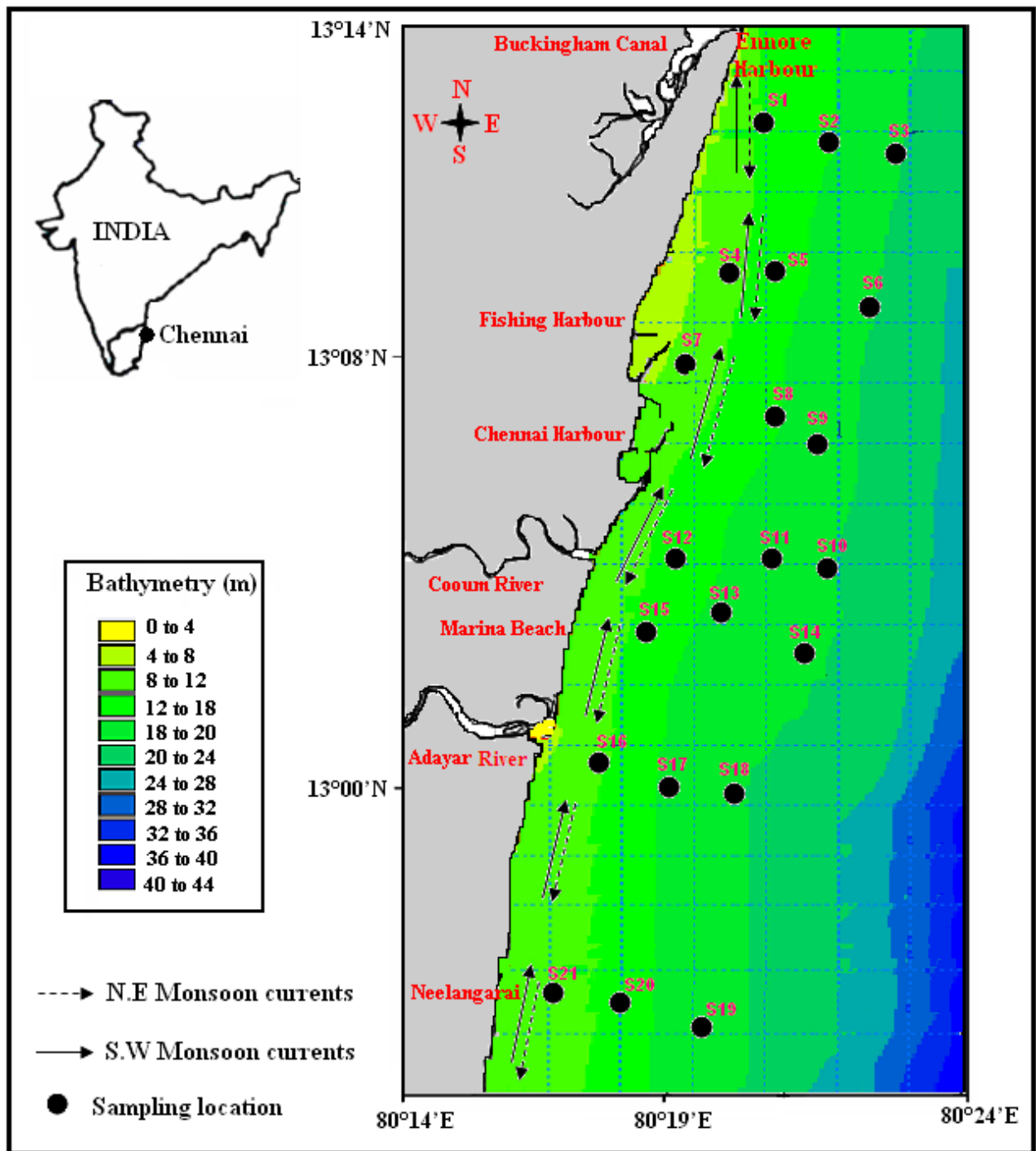


Figure 1: The study area and sampling locations.

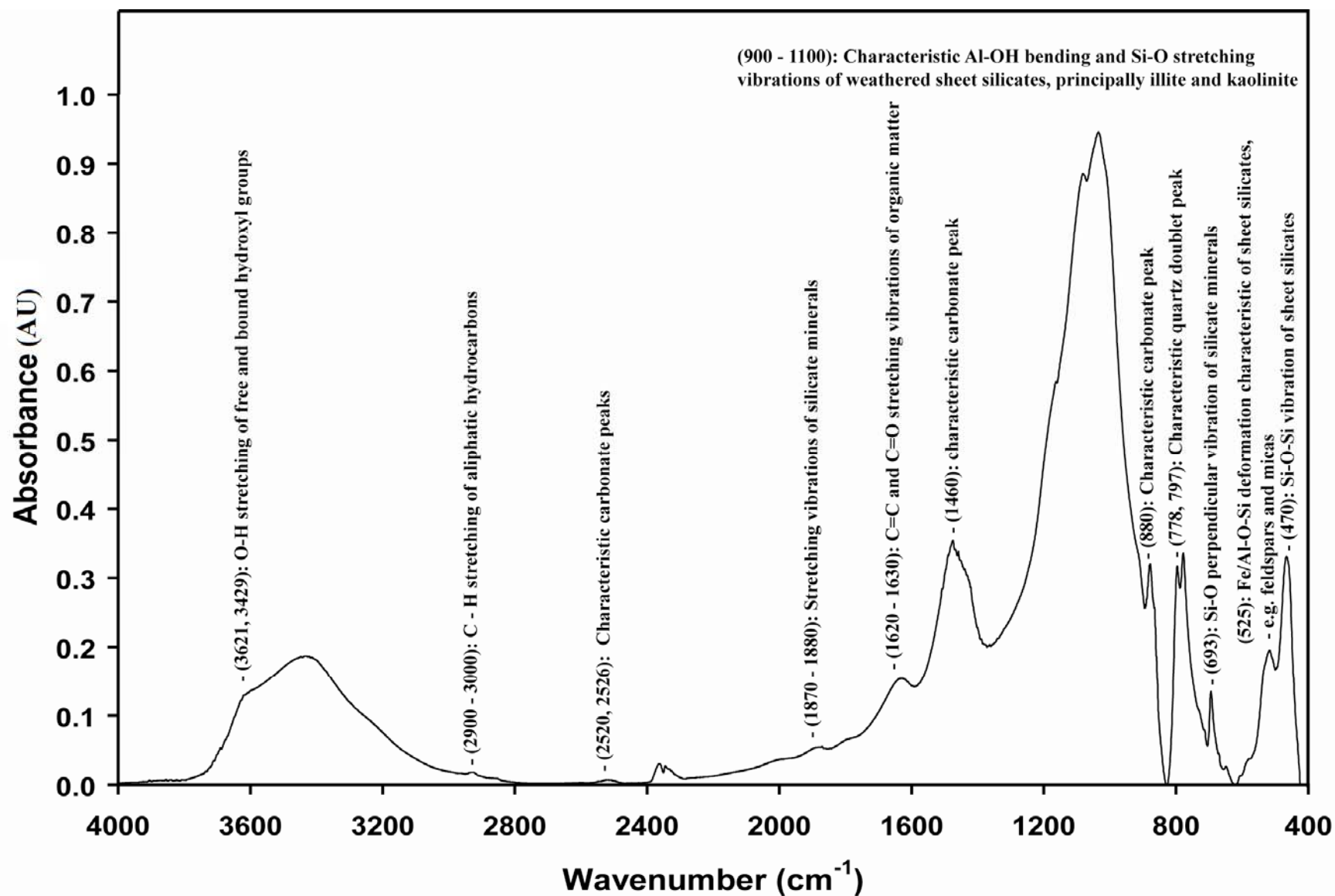


Figure 2: Representative FTIR spectrum of dried surface sediments collected off Chennai coast, Bay of Bengal, India.

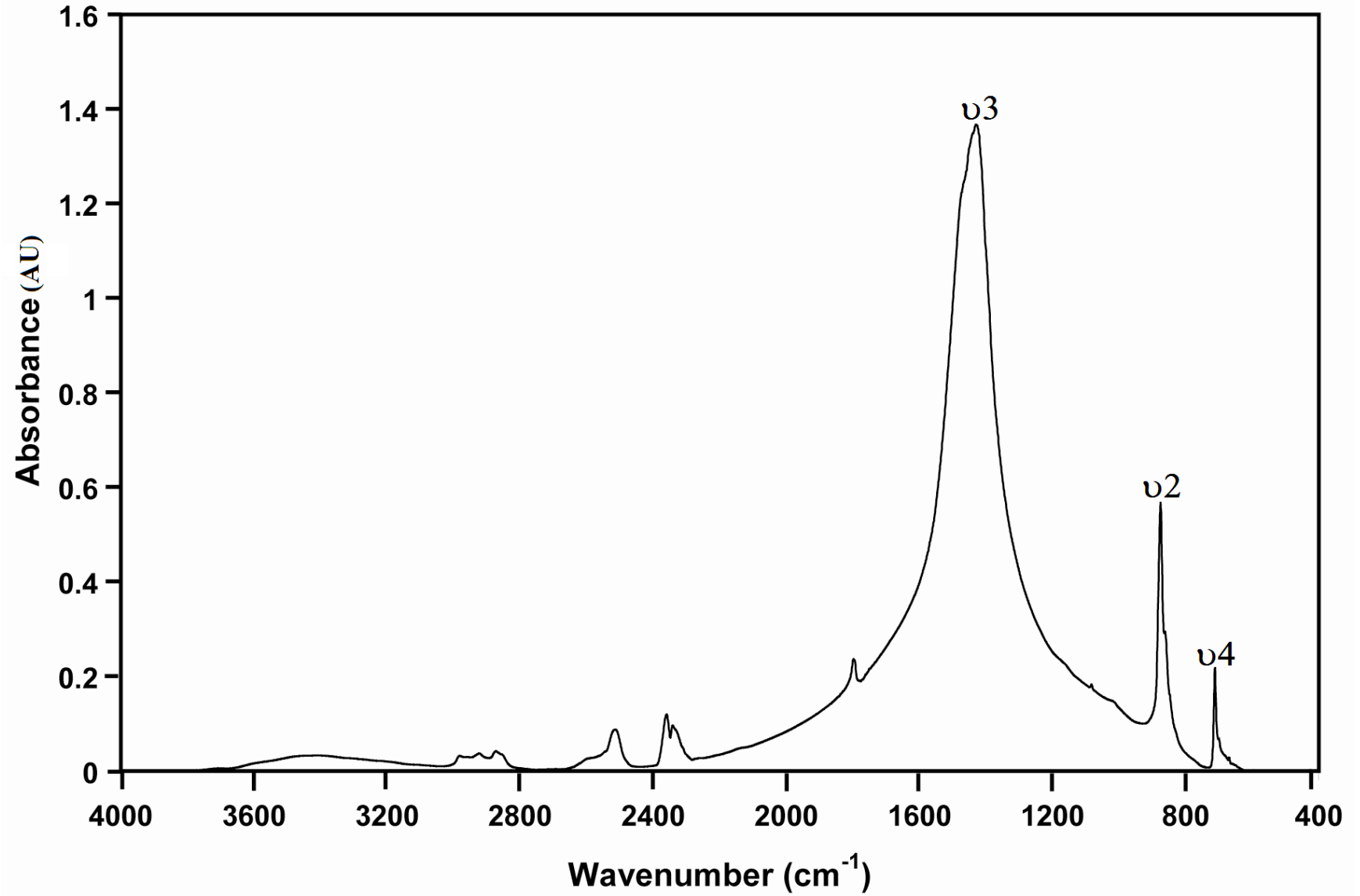


Figure 3: Infrared spectrum of pure CaCO₃.

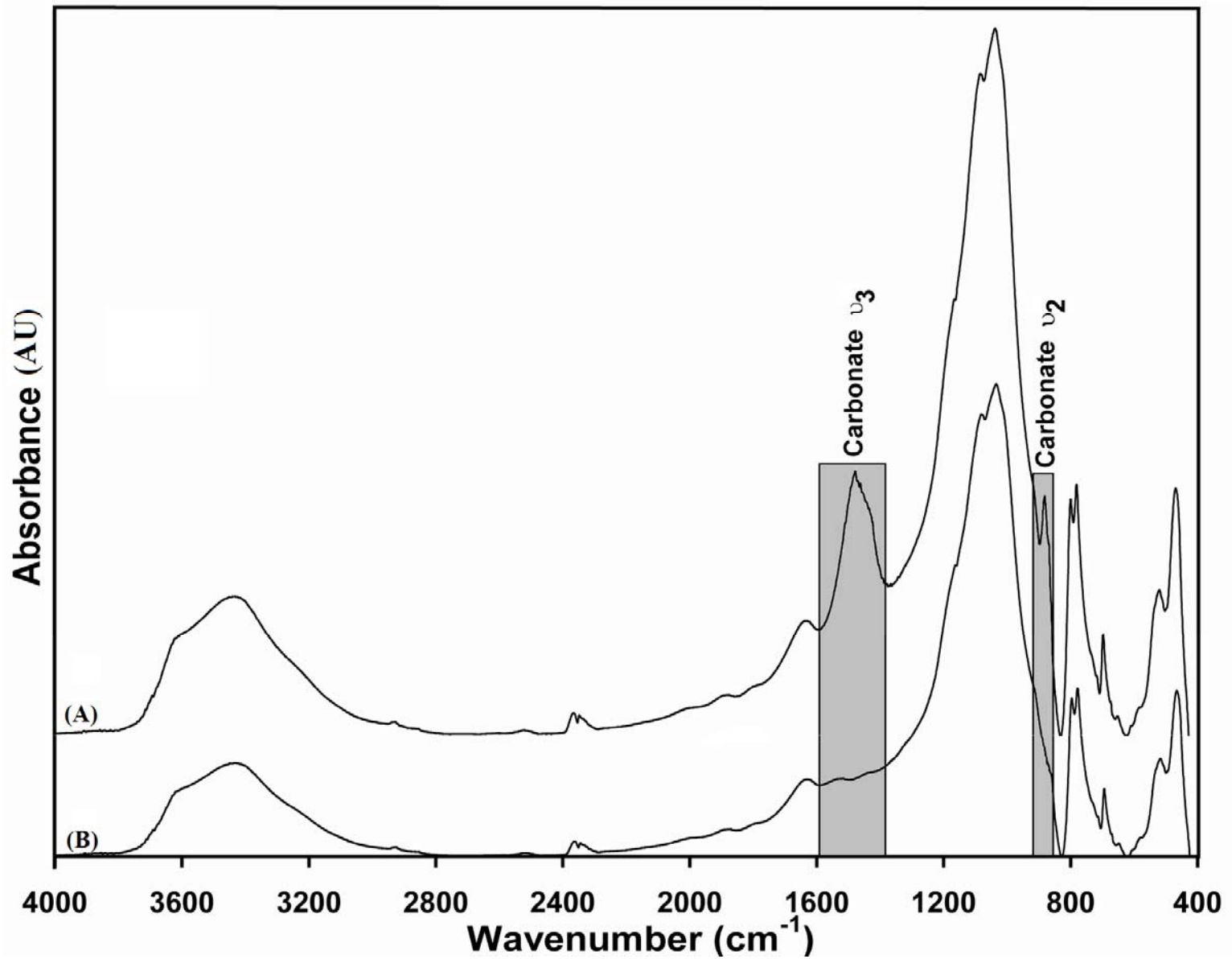


Figure 4: Comparison between the spectra of sample without any chemical treatment (A) and an HCl treated sediment sample (B).

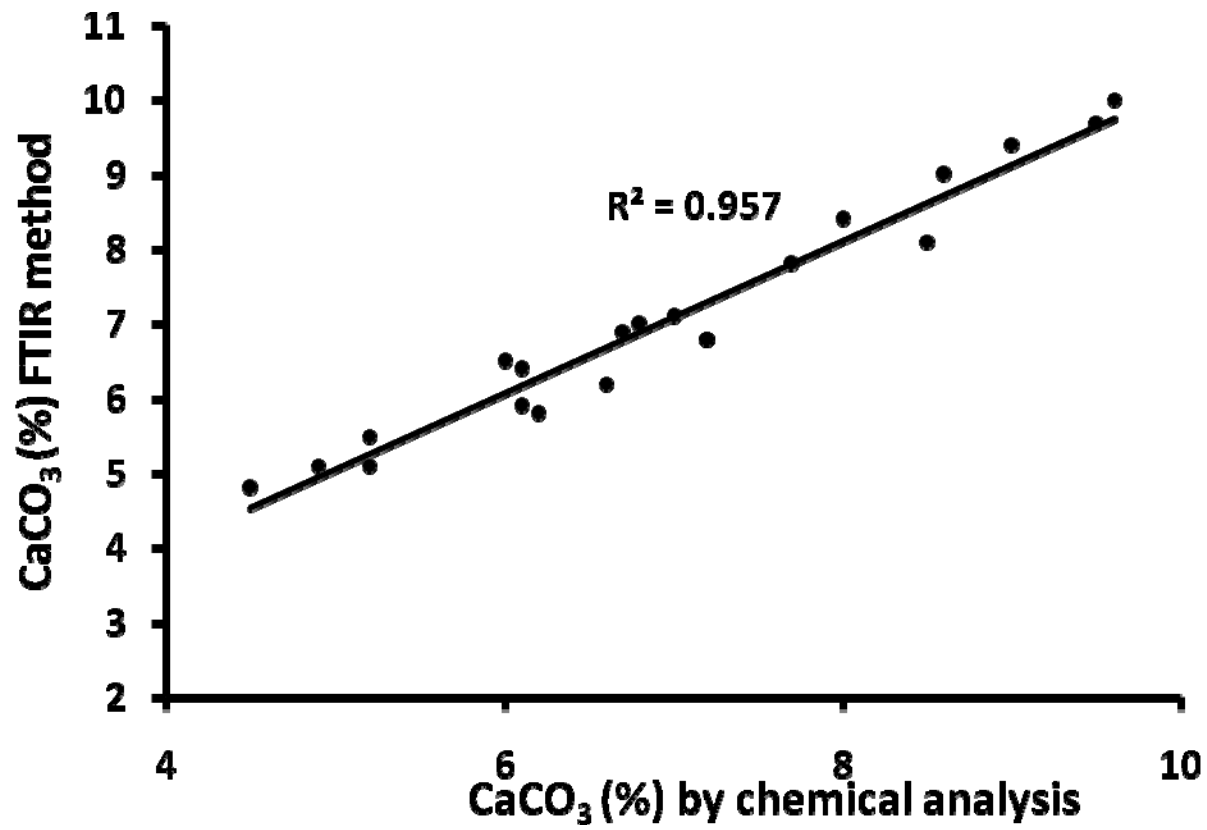


Figure 5: Correlation analysis between the carbonate results of FTIR and chemical analysis ($p < 0.05$).