



Research paper

Spontaneous oxygen isotope exchange between carbon dioxide and natural clays: Refined rate constants referenced to TiO₂ (anatase/rutile)



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ABSTRACT

In a series of our previously published papers, we reported a broad range of experiments and theoretical studies devoted to the interaction of carbon dioxide with the anatase titania surface. In the current study, we demonstrate oxygen mobility between gaseous carbon dioxide and solid natural clay minerals. This surprising feature implies that such behaviour is typical not only for titania but also for oxides with different chemical composition and structure. The oxygen mobility was demonstrated by the interaction of isotopically labelled carbon dioxide – C¹⁸O₂ – with the mineral surfaces. In most cases, we observed rapid oxygen exchange between the gas and the mineral. It was therefore discovered that carbon dioxide is more active than was previously thought because it exchanges its oxygen atoms with inorganic surfaces. Moreover, this feature seems to be very significant in natural clays of various compositions. This finding points not only towards high activity of CO₂ but also towards high surface reactivity of clays, which are quite common surface minerals on Earth and other planets.

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1. Introduction

It has long been known that carbon dioxide is adsorbed on many mineral surfaces (Udovic and Dumesic, 1984), such as soil and carbonate minerals (Hill et al., 2006; Rosenbaum et al., 1994), different types of oxides (Winter, 1968), titanium dioxide (Liao et al., 2002; Sorescu et al., 2011; Thompson et al., 2003), magnesium vanadate (Asedegbega-Nieto et al., 2005), magnesium oxide (Downing et al., 2014), aluminium oxide (Krupay, 1981), clays (Fanale and Cannon, 1979), nontronite, palagonite and basalts. The adsorption was studied because some of the minerals belong to the group of Martian regoliths (Babankova et al., 2006; Civiš et al., 2004; Fanale and Cannon, 1971; Ferus et al., 2014b, 2014c, 2009; Zent et al., 1994, 1987; Zent and Quinn, 1995), and it was hoped that the current atmospheric composition of Mars could at least partly be explained by those studies. In our previous studies (Civiš et al., 2015), we have shown that titanium dioxide (anatase {001} and {101}) is one of those minerals that interacts with carbon dioxide. We have also shown (Boháček et al., 1990; Civiš et al., 2015, 2014, 2013, 2011, 2012; Ferus et al., 2014a, 2009; Kavan et al., 2011; Purder et al., 1992) that CO₂ adsorbed on TiO₂ readily exchanges its oxygen atoms with the surface. This was elucidated by

monitoring ¹⁶O, ¹⁷O and ¹⁸O levels when isotopologues of carbon dioxide were used. The capacity to adsorb gases and interact reflects the mineral's considerably large internal surfaces (Bishop et al., 2002; Matthewman et al., 2015; Tokyryk and Civiš, 1995; Zent and Quinn, 1995).

The effectivity and the rate constants of the interaction are highly dependent on the nature of the TiO₂. In TiO₂ prepared from TiCl₄, the annealing process plays a major role. In samples where traces of HCl have been left at lower annealing temperatures, the effectivity of the exchange process was much smaller. When the annealing temperature is increased, however, the process occurs much more quickly and leads to higher yields. The annealing process results in the creation of oxygen defects on the surface. We have proposed this as the reason for the increased surface activity of the mineral (Sorescu et al., 2014). We have also shown that titania in the form of nanoparticles enhances this effect.

From this previous work, two main questions arose:

1. Do other minerals exhibit similar activity?
2. What is the role of residual HCl in the process, and why does carbon dioxide exhibit no traceable exchange activity in its presence?

In this work, we try to answer the first question. We monitored C¹⁸O₂, C^{18,16}O₂ and C¹⁶O₂ levels upon contact of C¹⁸O₂ with a series of mineral surfaces of clays containing a small amount of anatase (4–6%

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(w/w)). The clays all originated from the Sokolov Coal Basin in the Czech Republic. We then compared the results with previously published studies on basalt, calcite, siderite and synthetic and natural rutile and anatase. For this, we used a previously developed technique of high-resolution Fourier transform infrared spectroscopy (FTIR) of carbon dioxide isotopologues (Ferus et al., 2014a).

2. Materials and methods

2.1. FTIR spectroscopy

Our raw clay samples were gathered in the Sokolov Coal basin in the Czech Republic from former quarries. Natural anatase was obtained from Hordaland, Norway, and natural rutile from Golčův Jeníkov in the Czech Republic. Prior to any measurement, all clay samples were ground on a millstone-like grinding machine. Samples were then degassed and dried in vacuum (10^{-5} Torr) at a temperature of $100\text{ }^{\circ}\text{C}$ for six hours to enhance the degassing and drying process. The temperature of $100\text{ }^{\circ}\text{C}$ is not sufficient to make any changes in the surface structure. FTIR spectra were measured in a 30-cm long (2.5 cm in diameter) glass optical cell equipped with CaF_2 windows. The cell was interfaced to a sealable glass-tube joint for the in vacuo transfer of the powder material from a side ampoule, in which the annealing and degassing also occurred. In certain experiments, this in situ annealing was avoided. In such cases, the optical cell was simply loaded with the sample and evacuated. The optical cell was further equipped with a second vacuum valve (ACE glass, USA) for the gas handling and the connection to the vacuum line. The optical cell containing approximately 2 g of sample was filled with C^{18}O_2 (97% (v/v) ^{18}O , MSD Isotopes, Montreal, Canada, CAS 124–38–9). The pressure in the measuring cell was between 1 and 2 Torr and was precisely measured with an MKS Baratron pressure gauge (MKS Instruments, Inc., USA) (0–10 Torr). The spectral measurement was performed using a Bruker IFS 125 HR spectrometer (Bruker Optic, GmbH, Germany) (with a KBr beam splitter and a nitrogen cooled InSb detector) in the spectral range of $1800\text{--}6000\text{ cm}^{-1}$. The spectra were measured with a resolution of 0.01 cm^{-1} using the Blackmann–Harris apodization function (Ferus et al., 2008; Harris, 1978).

Concentrations of the various CO_2 isotopomers were determined by independent calibration using pure gases of defined isotopic ratios (carbon dioxide, 97% (v/v) ^{18}O , MSD Isotopes, 99.9995% (v/v) natural CO_2 ,

CAS 124–38–9, Linde Gas and a mixture of 0.39% (v/v) $\text{C}^{16,18}\text{O}_2$ and 98.42% (v/v) C^{16}O_2). The integrated areas under selected individual absorption lines were calculated using the OPUS 6.0 software package (Bruker Optic GmbH, Germany, 2006), and the data were subsequently fitted by a linear regression.

2.2. Brunauer-Emmett-Teller (BET) surface area measurement

The surface areas of the prepared materials were determined from nitrogen adsorption isotherms. The isotherms were recorded with an ASAP 2020 (Micromeritics, United States) volumetric instrument. To achieve the necessary accuracy for the accumulation of adsorption data, the instrument was equipped with three pressure transducers (13.3 Pa, 1.33 kPa and 133 kPa). The fresh samples were degassed by starting at the ambient temperature and heating to $80\text{ }^{\circ}\text{C}$ (temperature ramp of $0.5\text{ }^{\circ}\text{C}/\text{min}$) until a residual pressure of 1 Pa was attained. After further heating at $80\text{ }^{\circ}\text{C}$ for 1 h, the temperature was increased to $120\text{ }^{\circ}\text{C}$ (temperature ramp of $1\text{ }^{\circ}\text{C}/\text{min}$). At this temperature, degassing continued under a turbomolecular pump vacuum for 8 h. Adsorption isotherms of nitrogen were then recorded at $T = -196\text{ }^{\circ}\text{C}$ using a bath of liquid nitrogen.

The surface areas of the TiO_2 samples were calculated from the nitrogen adsorption data in a range of relative pressures (0.075–0.25) using the BET method.

An Iso-Therm thermostat (e-Lab Services, Czech Republic) was used to maintain the temperature of the sample with an accuracy of $\pm 0.01\text{ }^{\circ}\text{C}$ and was used for the measurement of carbon dioxide adsorption at $20\text{ }^{\circ}\text{C}$. As the adsorption isotherms of carbon dioxide were determined on the same sample immediately after the nitrogen adsorption measurement, the degassing procedure was performed at $120\text{ }^{\circ}\text{C}$ for 8 h with a turbomolecular vacuum pump.

The amount of adsorbed CO_2 on each sample was expressed in terms of cm^3 STP per m^2 of surface area calculated using the nitrogen isotherm.

2.3. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX) characterization

XRD was performed with a Bruker D8 Advance diffractometer (Bruker Optic, Germany). Samples were scanned with $\text{Cu K}\alpha$ radiation. SEM and EDX were carried out with a Hitachi S-4800 field emission

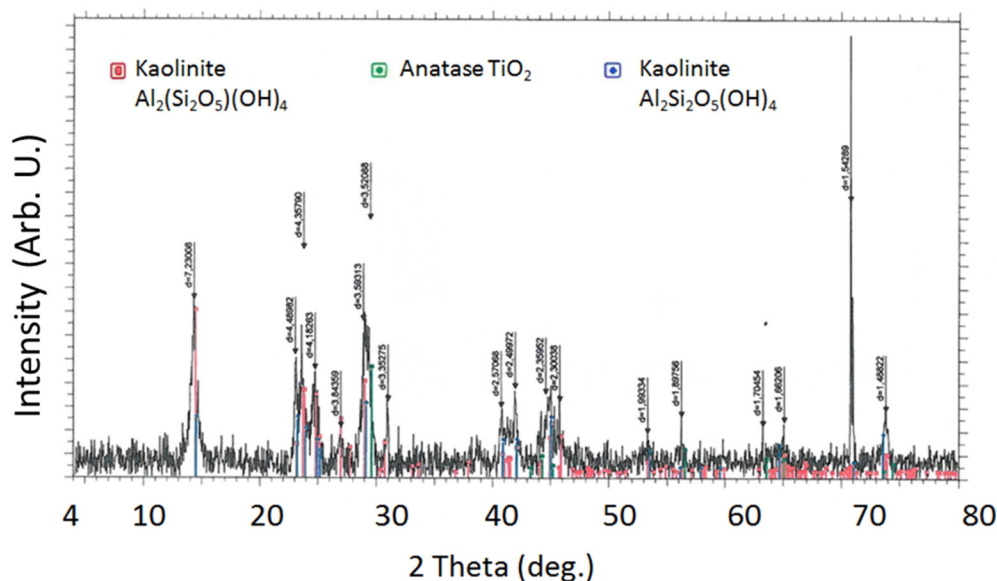


Fig. 1. X-ray diffraction analysis of S100-1 clay. Anatase and two types of kaolinite were identified as the main components of this sample.

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