Carbon dioxide and methane emissions from calcareous-marly rock under stress: experimental tests results

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Abstract

The identified emissions of abiogenic carbon dioxide, carbon monoxide and methane are generally attributed to volcanic activity or to geochemical processes associated with thermometamorphic effects. In this paper we show another possible abiogenic source of emission, induced by mechanical, and not thermal, stresses. We investigated the mechanochemical production of carbon dioxide and methane when friction is applied to marly-type rock and studied the mechanisms determining the strong CO_2 and CH_4 emissions observed. A ring mill was used to apply friction and oriented pressure upon a synthetic calcite-clay mixture of varying proportions. We found that the CO_2 and CH_4 release *versus* the grinding action has a non-linear trend reflecting the behaviour of decreasing crystallinity, which indicates a close link between crystallinity and gas production. For the CO_2 emission, we propose a release mechanism connected with the friction-induced fractures and the increase in structural disorders induced by creep in the lattice. The CH_4 emission could be explained by a Sabatier reaction in which CO_2 and hydrogen are involved to form CH_4 and water.

Key words *gas geochemistry – earthquake precursors – greenhouse gases*

1. Introduction

Numerous studies on the natural sources of greenhouse gases, such as methane and carbon dioxide, have been carried out in relation to the evolution of the Earth atmosphere as well as in the fields of geological and geochemical research. Our primary interest lies in the effects of greenhouse gases on the global climate. It is well-known that the greenhouse gas balance is evaluated according to three major sources of emission: abiogenic (volcanoes or thermometamorphism); non-anthropogenic biogenic (vegetation, earth, oceans) and anthropogenic.

Inorganic CO_2 emissions form a significant part of the total balance. The origin of this CO_2 concentration is generally attributed to volcanoes, geochemical cycles and thermometamorphic degassing produced by contact between carbonates and magma. Thermometamorphic generation of CO_2 has been discussed by Gianelli (1985), Marini and Chiodini (1994), Rogie *et al.* (2000), etc. Other greenhouse gases, such as abiogenic methane, are generally attributed to deep degassing.

Chiodini *et al.* (2000) estimated that thermometamorphic processes are responsible for about 36% of the CO_2 measured in Central Italy, while 41% comes from deep sources and 23% is biological.

Another interesting debate on the origin of greenhouse gases concerns the relationship between the greenhouse gas effect and the Cretaceous mass extinction. Many authors consider that the mass extinction of vertebrates at the end of the Cretaceous system was due to a meteorite impacting a carbonate basin; this induced the generation of enormous quantities of CO_2 through the dissociation of carbonates as an effect of the shockwave (Ryder *et al.*, 1996; MacLeod and Koeberl, 2001). However, the studies do not reach agreement on the mechanisms involved. Work on the carbonate compressibility by shockwaves shows how the CO_2 dissociation threshold varies from 10 to 60 GPa (Agrinier *et al.*, 2001; Skála *et al.*, 2001). According to other studies, carbonate dissociation could occur at much more limited pressures, but under certain stress conditions (Dickinson *et al.*, 1991).

A recent work demonstrated the possibility of obtaining an intense CO_2 emission from carbonate rocks with the contribution of mechanical energy by grinding alone (Martinelli and Plescia, 2004).

Methane is the subject of particular study, not only because of its environmental implications (greenhouse effect) but also in regard to its possible abiogenic origins of part of the oil reservoirs. A non-biogenic source of methane and more complex carbon composites could radically modify many of our current beliefs concerning the formation of oil and methane reservoirs (Beskrovny and Tikhomirov, 1968; Anders *et al.*, 1973; Porfir'ev, 1974; Kropotkin and Valyaev, 1976, 1984; Kropotkin, 1985).

Another important reason for studying the production/emission mechanisms of carbon dioxide and methane is the monitoring and prediction of seismicity for which there is general agreement on the importance of endogenic derived gases as possible precursors (*e.g.*, Irwin and Barnes, 1980; Geller, 1997; Toutain and Baubron, 1999).

The deformation processes that occurred in central Italy in 1997 and 1998 generated geochemical anomalies in the form of gas emissions and thermal springs within a 70 Km radius of the epicentre (Heinicke *et al.*, 2000; Favara *et al.*, 2001; Italiano, 2001). These geochemical anomalies can be grouped together as an impressive degassing process due to the variations in crustal permeability generated by deformation.

To study the CO_2/CH_4 emission from dynamic compression, it has been necessary to use a system that can induce a large amount of fracturing through strong compression and friction and with energy sufficiently high as to reduce crystallinity, *i.e.*, replicating what happens in rock during a strong tectonic activity.

2. Experimental

For laboratory work a ring mill was used, which is the most efficient grinding system available at present for the simulation of friction and mechanical compression over a large surface. Thanks to the mill we have (Martinelli and Plescia, 2004): a high exchange surface; high pressure on the materials; an isochemical ambient with controlled elementary exchange, and a high reaction rate.

The ring mill consists of a jar reinforced to contain the material and a grinding body (a steel ring and solid steel roller). A ring mill basically operates through non-hydrostatic compression (impact of the rings on the material particles) and friction (rotation forced by the grinding body on the particles and between the particles and the jar walls). Extremely high pressures can be achieved and complete amorphization of minerals with a Mohs hardness of less than 3-4 can be obtained within a few minutes (Plescia *et al.*, 2003). The exchange surface is very high as the pulverized material has very high specific surfaces and the quantity of material placed in the mill can exceed 10 g.

For our experimental trials we used a Labtech ESSA continuous ring mill conceived for continuous production of about 15 kg/h and modified to accommodate diagnostic instruments (fig. 1), *i.e.*, a konimeter to measure gas and dust and an analyzer for the internal temperature. Outside the grinding jar, a magnetic pickup connected to a digital oscilloscope provides data on the internal oscillations of the metallic mass, the grinding frequency and the dynamic events occurring during grinding (fig. 2).

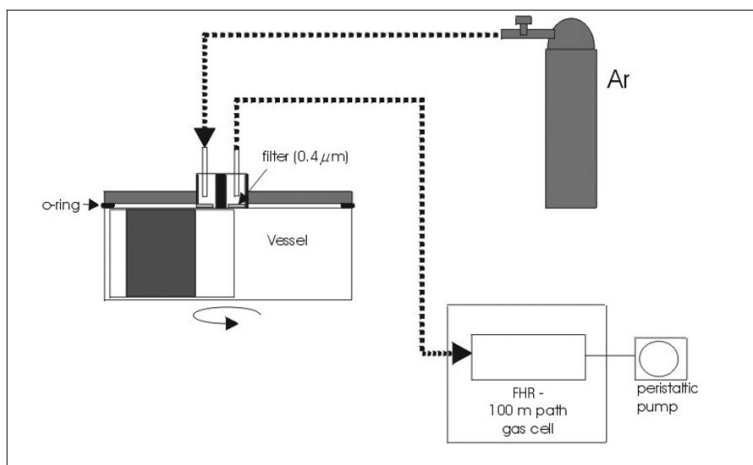The milled material consists of a mixture of pure calcium carbonate for analyses (Merck)

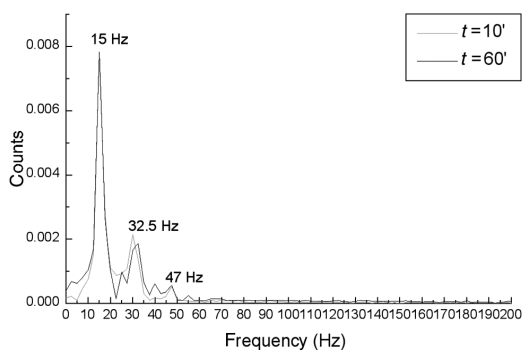**Fig. 1.** Layout of experimental apparatus.

Fig. 2. Fourier analysis of mill impact frequencies ad different grinding times.

Table I. Experimental conditions.

Grinding device: LABTECH ESSA
Jar material: steel
Grinding bodies: one 1 kg internal cylinder,
two 1.88 kg rings
Speed: 1200 rpm

FTIR - Gas cell experiment
FTIR: Nicolet Avatar 360
Sample cell: TGA thermostatic transfer line
and «100 m» long path cell
Carrier gas: argon, 99.9% pro analysis

X-ray diffraction: Rigaku Rint 1200
Anode: Cu, radiation Cu kα
Monochromator: Graphite crystal
Power supply: 30 kV-30 mA

Differential thermal analyzer:
Stanton 1500 DTA-TGA simultaneous analyzer
Reference α-Al2O3
Ramp in air from 25 to 1000°C at 5°/min

and kaolinitic clay. The clay sample, which was diffraction-analyzed before grinding, was found to be contaminated by quartz and a small quantity of illite.

Two types of tests were performed: for the first, non-stop grinding was carried out for 30, 60, 120 and 180 min on fixed amounts of 5 g; for the second, fixed-time grinding for samples of 2, 2.5, 5, 10 g was carried out.

The trials on samples of different grinding times and/or different weights allowed us to verify the effects of grinding with different amounts of energy per unit weight.

The mixtures were analyzed by TGA and DTA thermoanalyses to determine the amount of CO_2 released, the temperature and the

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amount of energy utilized in dissociation. The mixtures had a CO_2 content equal to 32% and an OH content equal to 6% (data obtained by differential thermal analysis).

We analyzed the gas using a FTIR spectrophotometer with «long path» thermostatic gas cells, similarly to what is used on GC/FTIR or TGA/FTIR systems. The instrument was a Nicolet Avatar 360. We used multiple acquisition software (Nicolet Omnic Series v.6.1A) to analyse the data in real-time and reproduce the reaction behavior. To analyze the gas in the jar and to avoid contamination from the outside, the jar was flushed with argon at a pressure of 1 bar. The gas flow was 0.5/min, controlled by an analogue flowmeter. For the *x*-ray diffraction and thermoanalyses, we used, respectively, a Rigaku Rint 1200 diffractometer and a Stanton STA 1000 thermal balance (table I).

3. Results

Practically all the CO_2 retained in marly rock was emitted in the grinding test. The quantity was slightly lower than that obtained by stoichiometry (about 20% as compared to the 22% obtained thermally), while methane, CO and H_2O were emitted in measurable quantities.

The phenomenon was confirmed by real-time analysis of the gas formed during grinding (figs. 3 and 4).

Figures 3 and 4 show the behaviour of the FTIR spectra in the vibration region of CO_2, methane and vapor as a function of grinding time for sample of a fixed weight. We can see that the CO_2 emission curve shows a complex behavior. There is a rapid increase at the beginning of the phenomenon, followed by a progressive decrease. During the experiment, the first two minutes are blank analyses, with the mill off, and no anomalous emission observed. The CO_2 emission effect is marked by peaks superimposed at a continuous level, while the methane appears after prolonged treatment, together with water (fig. 3).

Figure 5a,b shows a notable difference between thermal curves of the treated and as-is samples. The latter show three main reactions: weight loss due to evaporation of interstitial water (100-120°C); weight loss from dehydroxylation of clay, between 450-550°C, and weight loss related to the dissociation of CO_2 from calcite, between 700 and 900°C.

After grinding, the dehydroxylation peak, characteristic of the crystalline phase of clay, disappears; the dissociation peak of CO_2 decreases until it nearly disappears, from 35% for the as-is samples to 6% of the 180′ grinding
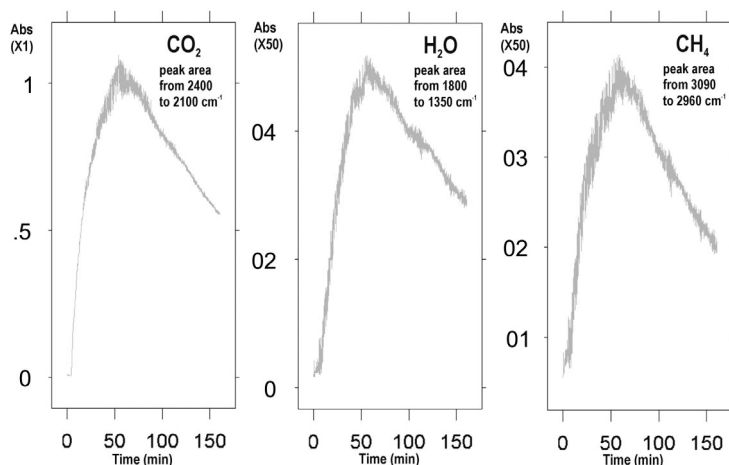

Fig. 3. FTIR Gas analysis: CO_2, H_2O, CH_4 emissions during milling (1 g sample, 180 min grinding).
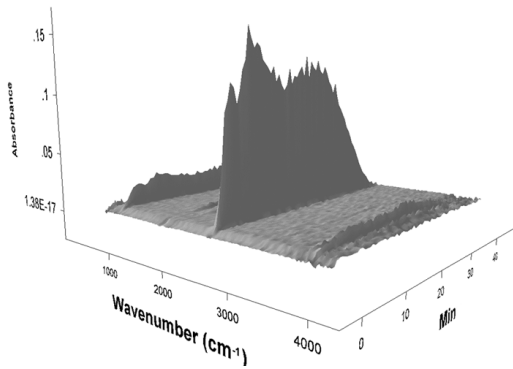
Fig. 4. 3D view of FTIR spectra (1 g sample).

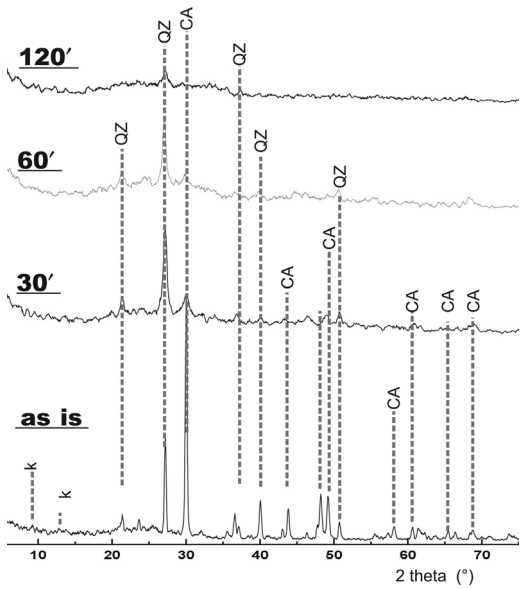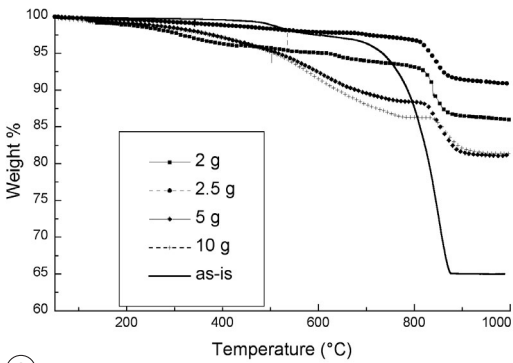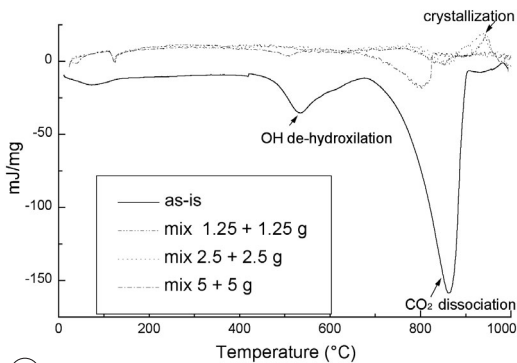**Fig. 5a,b.** Thermal analysis of ground samples: a) TGA analysis; b) differential thermal analysis.

Fig. 6. XRD analysis of treated samples at different main grinding time phases: QZ – quartz; k – kaolinite; CA – calcite.

samples, and a crystallization peak appears at very low temperatures. The vitrification temperature, for a mixture calcite/kaolinite clay as is, is around 1300-1400°C.

In the grinded samples this temperature is placed at 1100°C. Figure 6 shows the *x*-ray diffraction analysis of grinded samples at different grinding times. The XRD shows how the treatment leads to amorphization of the calcite and clay minerals. In particular, calcite tends to amorphous product, instead of crystallize as aragonite, as observed in previous experiments on calcite single crystal grinding (Martinelli and Plescia, 2004).

In the 120′ sample, it can be observed only the main reflections of quartz, which constitutes the hardest phase of the mixture.

4. Discussion of results

The most noteworthy data are related to the modality and typology of emission, which can

be attributed to the mechanical, and not the thermal, phenomenon imposed on the marly material.

Worth noting, firstly of all, are the CO_2 emissions, which we have explained in terms of two parallel mechanisms: burst emissions, due to the release of CO_2 molecules from fresh grinding-induced fractures; and continuous emissions, deriving from the bulk, *i.e.*, produced by the material which is not yet fractured, but is undergoing compression and micro-cracking (plastic deformation, slippage of planes).

Burst emissions seem to be prevalent only during the very early grinding phases, while continuous emissions become dominant after a few minutes' treatment. The phenomenon of continuous CO_2 emission brings us to conclude that the deformed lattice of the carbonate releases CO_2 up to equilibrium. Instead water and methane emissions originate in a different scenario. In fact, we suggest that the methane and water derive from the Sabatier reaction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O.$$
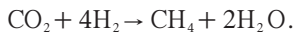
This reaction is moderately exothermic, $H° = -165$ kJ/mol, and could originate when hydrogen molecules become available during grinding. The protonization event coincides with dehydroxylation of the clay during the grinding of the mixture. Several authors (Aglietti *et al.*, 1986; Plescia *et al.*, 2003) have clearly demonstrated that phyllosilicates are particularly sensitive to the mechanochemical action, which easily leads to the elimination of the OH groups and to a completely amorphous structure. It is also well-known that clays, particularly kaolinite, are capable of exchanging protons with the external ambient, but only half of the available protons are exchangeable with a simple high-*pH* reaction, while acid or neutral *pH* exchange is not viable.

The phenomenon could evolve as follows: during the first grinding phase (or friction action), the material is fractured and the calcium carbonate releases carbon dioxide with spot emission; then, the CO_2 emission becomes abundant and continuous, while the chemical ambient becomes strongly alkaline; the clays are destroyed by grinding and lose hydroxyls

and, hence, protons, some of which recombine with CO_2 molecules to give rise to methane and water – both observable in the FTIR gas spectra; at the end of the grinding, the CO_2 emission tends to very slowly decrease up to re-equilibrium of the material.

To verify our hypothesis, the role of energy during grinding needs to be carefully evaluated. By using the mathematical model developed to study the ring mills (Plescia, 2003), we calculated that the energy provided by the mill is about 1240 kJ/h (345 J/s). This energy is subdivided by the amount of material put in the mill. The energy generated would be sufficient to complete the reaction, and the chemical ambient is alkaline enough to guarantee de-protonization of the clay.

It is also worthwhile recalling a particular mineralogical fact: in some minerals present in certain metapelites, such as cordierite, significant quantities of hydrocarbons derived from methane were revealed by IR (Mottana *et al.*, 1983; Khomenko and Langer, 1999). The presence of methane and related hydrocarbons could be associated with gas formation during metamorphic events.

5. Conclusions

The data obtained so far allow us to put forward the following hypotheses: in addition to the known mechanisms involved in CO_2 and methane production, there exists a natural mechanism that works through a mechanochemical-type phenomenon; an abundant amount of CO_2 is produced during shear stress by mechanochemical molecular dissociation of calcium carbonate; the energies involved are sufficient to dissociate carbonate, so long as there is a very high grinding body/material ratio; the amount of shear stress necessary to obtain the dissociation of CO_2 and production of CH_4 is less then 4 kbar, the threshold value to obtain the crystallization of aragonite.

The phenomenon observed in the laboratory could be tentatively extrapolated to a much larger scale so as to give us some idea of what actually happens when carbonate-rock mass undergoes tectonic activity.

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