



Petrology, geochemistry (Mineralogy)

CO<sub>2</sub> geological storage: The environmental mineralogy perspective*Minéralogie environnementale et stockage géologique de CO<sub>2</sub>*François Guyot <sup>a,\*</sup>, Damien Daval <sup>a,c,d</sup>, Sébastien Dupraz <sup>a,e</sup>, Isabelle Martinez <sup>a</sup>, Bénédicte Ménez <sup>a</sup>, Olivier Sissmann <sup>a,c</sup><sup>a</sup> Équipe de recherche technologique, stockage géologique de CO<sub>2</sub>, université Paris-Diderot and Institut de Physique du Globe de Paris (IPGP), 1, rue Jussieu, 75005 Paris, France<sup>b</sup> Institut de minéralogie et de physique des milieux condensés (IMPMC), 4, place Jussieu, 75005 Paris, France<sup>c</sup> UMR 8538 du CNRS, laboratoire de géologie, École normale supérieure, 24, rue Lhomond, 75005 Paris, France<sup>d</sup> Lawrence Berkeley National Laboratory, Earth Sciences Division, Berkeley, USA<sup>e</sup> BRGM, 3, avenue Claude Guillemin, 45000 Orléans, France

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## ABSTRACT

Geological storage of carbon dioxide (CO<sub>2</sub>) is one of the options envisaged for mitigating the environmental consequences of anthropogenic CO<sub>2</sub> increases in the atmosphere. The general principle is to capture carbon dioxide at the exhaust of power plants and then to inject the compressed fluid into deep geological formations. Before implementation over large scales, it is necessary to assess the efficiency of the process and its environmental consequences. The goal of this paper is to discuss some environmental mineralogy research perspectives raised by CO<sub>2</sub> geological storage.

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## RÉSUMÉ

Le stockage géologique du CO<sub>2</sub> constitue une des options envisagées pour faire face aux conséquences environnementales de l'augmentation de la concentration atmosphérique en dioxyde de carbone. Le principe général repose sur la capture du CO<sub>2</sub> en sortie des centrales électriques, suivie de son injection sous pression dans des formations géologiques souterraines. Avant une éventuelle application à grande échelle, l'efficacité de ce procédé ainsi que ses conséquences environnementales doivent être évaluées. Le but de cet article est de discuter quelques perspectives de recherche en minéralogie environnementale soulevées par le stockage géologique du CO<sub>2</sub>.

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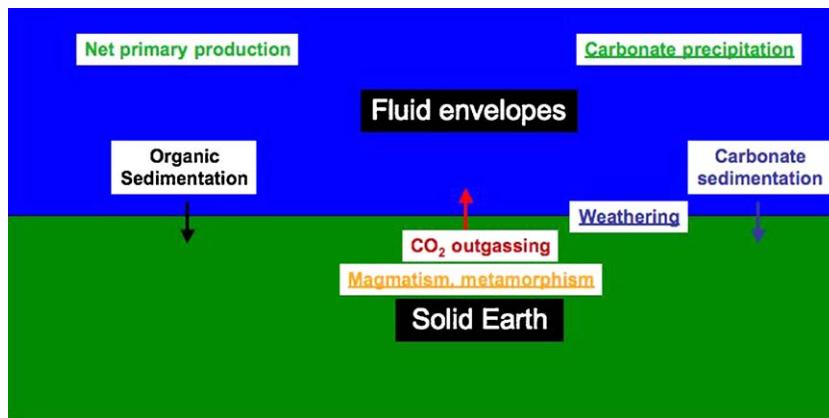
1. Mineralogy of CO<sub>2</sub> geological storage

Before thinking of manipulating carbon dioxide (CO<sub>2</sub>) at a large scale (which mankind has done already by burning

large quantities of fossil fuels), it is useful to have a coherent view of the natural CO<sub>2</sub> geochemical cycle. This will allow assessment of the extent of environmental anthropogenic perturbation and identification of the mineralogical mechanisms of interaction of carbon dioxide with its surrounding. A general scheme of the CO<sub>2</sub> cycle without anthropogenic perturbation is given in Fig. 1 with

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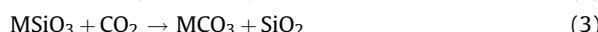
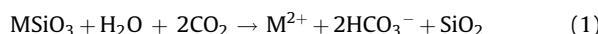


**Fig. 1.** Schematic representation of the CO<sub>2</sub> natural cycle in the mode of geochemical boxes. Arrows are indicative of fluxes of the order of 10<sup>13</sup> moles of carbon per year. Weathering (alteration of minerals at the interface between solid Earth and fluid envelopes) and net primary production (essentially photosynthesis minus respiration on a global scale) are natural mechanisms of capture of CO<sub>2</sub> outgassed from the solid Earth by magmatic and metamorphic processes. Processes in which mineralogical control is primordial are underlined.

**Fig. 1.** Représentation schématique du cycle naturel de CO<sub>2</sub> sous forme d'échanges entre réservoirs géochimiques. Les flèches représentent des flux de l'ordre de 10<sup>13</sup> moles d'atomes de carbone par an. L'altération (réaction chimique des minéraux à l'interface entre la Terre solide et les enveloppes fluides) et la production primaire nette (essentiellement le bilan global photosynthèse-respiration) sont des mécanismes naturels qui permettent de capturer le CO<sub>2</sub> dégazé depuis l'intérieur de la Terre par magmatisme et métamorphisme. Les processus dans lesquels la minéralogie joue un rôle primordial sont soulignés.

emphasis on the main processes where mineralogical science will be most useful. More detailed representations of the carbon cycle can be found elsewhere (e.g., Gaillardet and Galy, 2008). In a simplified view, one considers generally that the flux of outgassing of CO<sub>2</sub> from the solid Earth by magmatic and metamorphic processes is of the same order of magnitude as that of its export to the solid Earth in the form of carbonate minerals and of fossil organic matter. The feedback mechanisms within this cycle are still unclear and constitute the object of intense research (e.g., Berner, 1991; Gaillardet and Galy, 2008). Two major non-mutually exclusive hypotheses for these mechanisms are considered:

In the first, the alteration rate of minerals is indirectly correlated to CO<sub>2</sub> contents of the atmosphere and hydrosphere (see a review in Kump et al., 2000) through temperature variations, erosion rates, role of vegetation, soil pressure of CO<sub>2</sub>, etc. The main chemical reactions involved in the alteration of minerals and subsequent precipitation of carbonates are summarized as dissolution of silicates (reaction (1)), precipitation of carbonates (reaction (2)), and capture of CO<sub>2</sub> by chemical weathering (reaction (3)), which represents the sum of reactions (1) and (2)):



In these chemical reactions, only silicates with divalent M cations such as Mg<sup>2+</sup> and Ca<sup>2+</sup> are represented, but dissolution reactions can also be written with monovalent cations (Na<sup>+</sup>, K<sup>+</sup>). However, for crystal chemical reasons, alkali cations are rarely involved in solid carbonate precipitation and thus in the global export of CO<sub>2</sub> to the solid Earth (e.g., Oelkers et al., 2008). Conversely, such

cations could be involved in reverse weathering on continental margins and are actually thought to potentially reduce the uptake of CO<sub>2</sub> from mineral weathering (Mackenzie and Kump, 1995).

Positive feedback between the thermodynamic activity of CO<sub>2</sub> and silicate dissolution is not easy to demonstrate, and the governing mechanisms are not well established. For example, positive temperature-silicate dissolution correlations have been demonstrated in the case of basalts (Dessert et al., 2003; Gaillardet et al., 1999) and suggested for granites (White and Blum, 1995). Of course, understanding in detail the mineralogical aspects of silicate dissolution and of carbonate precipitation is an essential component required for understanding that regulation.

The second hypothesis involves photosynthesis by bacteria, photosynthetic unicellular eukaryotes and green plants, as represented simplistically by reaction (4), which represents primary production via photosynthesis:



Oxygenic photosynthesis is enhanced as carbon dioxide increases, either through temperature increase or because of CO<sub>2</sub> limitations of biomass in some ecosystems. The reverse reaction



which represents respiration and combustion of biomass, is also enhanced. However, because some of the organic matter unavoidably escapes as it is transformed into refractory phases (the term refractory will be used here for organic matter resistant to biological respiration and fermentation), the difference [(4)–(5)], namely, the global net primary production, is positive. Then, either directly (by sedimentation in the ocean) or indirectly (by transport of soil refractory organic matter to the ocean and then sedimentation), some CO<sub>2</sub> is transferred to the solid Earth.

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