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Carboxylate anion generation in aqueous solution from carbonate radiolysis, a potential route for abiotic organic acid synthesis on Earth and beyond

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ABSTRACT:

Low molecular weight carboxylate anions such as formate (HCOO^-), acetate (CH_3COO^-) and oxalate ($\text{C}_2\text{O}_4^{2-}$) have been shown to play an important role in supporting deep subsurface microbial ecosystems. Their origin whether biological or abiotic is currently highly debated, but surprisingly radiolytic production has rarely been considered, as it is the case for H_2 . Here, we address this question through dedicated irradiation experiments. Aqueous solutions containing carbonate, formate, acetate or oxalate have been irradiated using both the 60.7 MeV α -beam of the ARRONAX cyclotron (Nantes, France) and 661.7 keV γ -Ray in order to reveal the mechanism and chemical yield of radiation-induced dissolved carbonate degradation.

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The yields (G-values) of carboxylate anions production/degradation in low-concentration carbonate solution (0.01 to 1 mmol L⁻¹) are measured. Carbonate degradation occurs through three consecutive steps (Carbonate $\xrightarrow{I}$ Formate $\xrightarrow{II}$ Acetate $\xrightarrow{III}$ Oxalate) involving formate radical (CO₂^{•-}), dihydrogen (H₂), and carbon dioxide (CO₂) generation. Dissolved carbonate radiolysis provides a consistent pathway for both enhancing two-fold the radiolytic H₂ production compared to pure water and generating carboxylic species, chiefly oxalate, readily available for microbes. Radiation-induced carbonate degradation may produce substantial amount (millimolar concentration) of carboxylate anions in ancient groundwaters from deep crystalline bedrocks. Subsurface lithoautotrophic microbial ecosystems may not only be supported by radiolytic H₂ but also by carboxylate species from carbonate radiolysis. Carbonate radiolysis can be also an endogenous source of carboxylate species on Mars and other planetary bodies.

1. Introduction

Abiotic organic synthesis is central to life emergence, deep subsurface microbial activity, and global geochemical carbon cycling (Ménez 2020, Truche et al. 2020). Currently, there are two major sources of abiotic organic compounds envisioned on Earth. First, they could be mantle sourced and supplied to the crust through the migration of magmatic fluids (Sephton and Hazen 2013). Second, they could be formed within the crust through reduction of inorganic carbon compounds such as carbonates or CO. This latter process is supposed to be triggered by water-rock reactions involving molecular hydrogen (H₂) and catalyst surfaces (McCollom 2013, Seewald 2001). Molecular hydrogen may be produced abiotically by the reduction of water in the presence of Fe(II)-bearing minerals, by reaction of FeS (pyrrhotite) with water to generate FeS₂ (pyrite) plus H₂, or even by the reaction of water with surface radicals during mechanical

43 fracturing of silicate-bearing rocks (Klein et al. 2020). Water radiolysis due to radioactive decay
 44 either by α -emitters such as U and Th or γ -Ray emitter such as K^{40} is also considered as an
 45 important source of H_2 in the Earth's crust (Lin et al. 2005, Sherwood Lollar et al. 2014).
 46 Among the abiotic organic compounds potentially produced at depth, the low molecular weight
 47 organic acids, such as formate and acetate, have attracted particular attention as they have been
 48 shown to play an important role in supporting deep microbial communities, either in serpentinite-
 49 hosted environments (Fones et al. 2019, Lang et al. 2018) or in deep crystalline bedrocks
 50 (Bomberg et al. 2016, Hoehler and Jørgensen 2013, Purkamo et al. 2017). Even if the abiotic
 51 nature of their sources is still a matter of intense debate, the rationale for carboxylate anions
 52 formation during carbonates radiolysis in aqueous solution remains currently ignored in these
 53 natural and undisturbed geological settings (Sherwood Lollar et al. 2021). A radiation-induced
 54 source of carboxylate anions would be particularly relevant in Precambrian Shield environments
 55 because of the high dose deposited in deep fracture fluids, which results from both the long
 56 residence time of groundwaters and the radioactive decay of U, Th, and K enriched within the
 57 rock matrix (Holland et al. 2013, Warr et al. 2019).
 58 Carboxylate anions (formate $HCOO^-$, oxalate $C_2O_4^{2-}$, glyoxylate $(HO)_2CHCO_2^-$, glycolate
 59 $C_2H_3O_3^-$ and acetate CH_3COO^-) are the main organic products during carbonate-bearing aqueous
 60 solutions radiolysis (Cai et al. 2001, Costagliola et al. 2017, Draganić et al. 1991). Although the
 61 radiation chemistry of carbonate-bearing solutions has been extensively studied within the
 62 framework of nuclear waste geological disposal, there is a still major uncertainty regarding: i)
 63 the reaction mechanisms, ii) the respective yield of each carboxylate species, and iii) the Linear
 64 Energy Transfer (LET) effect (i.e. the amount of energy that an ionizing particle transfers to the
 65 material traversed - here water - per distance unit). A detailed understanding of the mechanism

and yield of radiolytic carboxylates production is necessary to constrain their concentrations in natural groundwaters and assess their importance as carbon sources for the deep subsurface biosphere.

To fill this gap, we studied the behavior of radiolytic carbonate degradation products as a function of the dose deposited into low-concentration carbonate aqueous solutions (0.01 to 1 mmol L⁻¹) representative of ancient groundwaters from deep crystalline bedrocks (Bomberg et al. 2016, Kieft et al. 2018, Pedersen and Ekendahl 1992, Sherwood Lollar et al. 2021). We quantified the production/degradation of each species: carbonate (CO₂/HCO₃⁻/CO₃²⁻), molecular hydrogen (H₂), formate (HCOO⁻), acetate (CH₃COO⁻) and oxalate (C₂O₄²⁻) ions. In addition, we investigated for the first time the LET effect by comparing γ -Ray experiments with newly performed high energy helium ion (He²⁺ = α -beam irradiation) ones. The measured carboxylates production yields were used to calculate their long-term production in natural settings and discuss their potential role in supporting deep microbial ecosystems.

2. Carbonate radiolysis and recombination of radical species

During the irradiation of carbonate solutions, water radiolysis byproducts (e_{aq}⁻ = aqueous electron with water coordination (H[•], HO[•], H₂, H₂O₂, H₃O⁺) react with CO₂, CO₃²⁻ and HCO₃⁻ and produce CO₂^{•-} and CO₃^{•-} radicals according to:

Where k is the rate constant of the reaction in L mol⁻¹ s⁻¹.

85 These radicals mainly recombine with each other or react with other radical species produced by
 86 water radiolysis. The following reactions lead to the formation of carboxylate ions such as
 87 oxalate and formate :

88 The radiation chemical behavior of formate has already been the subject of several studies
 89 (Albarrán et al. 1987, 1994, Cai et al. 2001, Costagliola et al. 2017, Draganić et al. 1991). The
 90 main formate (or formic acid) degradation reaction by water radiolysis products are the
 91 following:

92 Recently, we have discussed the impact of ionizing radiations (α -beam and γ -Ray) on calcite and
 93 calcium carbonate solutions (Costagliola et al. 2017). We have shown that calcite dissolution is
 94 accompanied by organic anions formation such as formate, acetate and oxalate ions. However,
 95 whereas the formate and oxalate ions production has been previously described in the literature,
 96 (Draganić et al. 1991), the acetate production mechanism remains not well-understood.
 97 Moreover, for these carboxylate anions, no unquestionable quantification was proposed for their
 98 production/degradation radiolytic yield. Albarrán et al. 1987, 1994 have observed acetate
 99 formation following γ -Ray of calcite, but without clear explanation. Cai et al. 2001 have
 100 accurately determined the chemical yield of oxalate ($G_{\gamma}(\text{C}_2\text{O}_4^{2-}) = 2 \text{ nmol J}^{-1}$) at high
 101 concentration of bicarbonate (50 mmol L^{-1}) in aqueous solution, but without acetate and formate

quantification. Here, we perform a complete measurement and quantification of the carboxylate ions behavior during dissolved carbonate radiolytic degradation under both α -beam and γ -Ray.

3. Experimental methods

3.1. Sample sets and analytical procedures

All the aqueous solution used in the experiments were prepared with commercial chemical products as received with no further purification. All reactants were analytical grade and the aqueous samples were prepared with ultrapure (MilliQ) water. A summary of each experiment with the values of parameters used is given in **Table 1**. All the experiments have been carried out at $21 \pm 1^\circ\text{C}$. Carboxylate-bearing experiments were performed under aerated condition and initial pH = 7.0. At such a pH value, the carboxylate anions predominate in solution. Carbonate-bearing experiments were performed under Ar atmosphere and initial pH = 10 to avoid CO_2 degassing. In the present case, the atmosphere composition (air vs. Ar) has no significant impact on the mass balance of the reaction as described by Costagliola et al. 2017. Dissolved concentrations of carboxylate and carbonate anions fall within a representative range of natural groundwater (0.01 to 1 mmol L^{-1}).

Molecular hydrogen (H_2) and carbon dioxide (CO_2) have been monitored by micro gas-chromatography (μGC) using a 490-GC (VARIAN[®]) micro gas-chromatograph. Two columns were used: a 5 Å molecular sieve for H_2 and a poraplot Q for CO_2 . The injection system and the column were purged with argon beforehand. Carboxylate anions concentration was determined by ionic chromatography using a METROHM 850 pro IC chromatograph with a Metrosep ASUP16 column. This column was thermostated at 55°C and a 75 mmol L^{-1} Na_2CO_3 + 0.75 mmol L^{-1} NaOH eluent was chosen. Finally, carbonate anions concentration was determined

using a DIONEX[®] chromatograph with a DIONEX[®] IonPac AS18 column and 0.25 mmol L⁻¹ NaOH eluent. All our chromatographic measurements (both IC and GC) were repeated 3 times, with a precision of 3% at the 95 % confidence level. All the analytical results are reported in supplementary Table S1.

Table 1. Summary of experimental conditions used in this work

#Sample Name	Initial Solution	Initial Conc. mmol L ⁻¹	Radiation	Total Dose (Gy)	Irradiation Time (min)
He-Carb	Carbonate	0.2	α -beam	5600	8
G-Water	MilliQ water	-	γ -Ray	1434	180
G-Form	Formate	0.01	γ -Ray	1900	240
G-Ac	Acetate	0.01	γ -Ray	1780	220
G-Ox	Oxalate	0.01	γ -Ray	1900	240
He-High-Form	Formate	1	α -beam	10500	15
He-Low-Form	Formate	0.01	α -beam	10500	15
He-High-Ac	Acetate	1	α -beam	10500	15
He-Low-Ac	Acetate	0.01	α -beam	10500	15
He-High-Ox	Oxalate	1	α -beam	10500	15
He-Low-Ox	Oxalate	0.01	α -beam	10500	15

3.2. Irradiation experiments

γ -Ray and α -beam irradiations experiments were performed at the ARRONAX cyclotron (Nantes – France) facility. The irradiation cells were made of PEEK (polyether ether ketone), mounted with a rotulex 19/9 glass tube and had an internal volume of 41 mL or 42 mL for α and γ cells,

respectively. These cells were gas-tightened using a screwed silicone seal joint in a glass-metallic valve. The specificity of each experiment is discussed thereafter.

3.2.1. α -beam irradiation

The initial energy of the ARRONAX α -beam was 68 MeV. The PEEK irradiation cell was equipped with a 150 ± 15 μm thick borosilicate glass disk as entrance window in order to minimize energy losses as ions enter the cell. The SRIM2008 simulation code developed by Ziegler et al. 2010 demonstrated that the particle energy on the other side of the entrance window is 60.7 ± 0.3 MeV. 20 mL of solutions at the desired concentration were loaded inside the cell. Stirring of the solution was performed to ensure a homogenous irradiation of the medium. Fricke dosimetry (Fricke and Hart 1966) was performed by *in situ* monitoring of the ferric ion concentration with CARY-4000 (VARIAN[®]) spectrophotometer, coupled to a 20 m long fiber optics and a 10 mm optical path HELMA[®] probe. This setup is described in supplementary Figure S1. Therefore, the ferric ion radiolytic yield used for this α -beam was $G_{\alpha}(\text{Fe}^{3+}) = 1.17$ $\mu\text{mol J}^{-1}$.

3.2.2. γ -Ray irradiation

γ -Ray irradiation was performed with a GSM D1 (Gamma-Service Medical[®]) irradiator containing a 123 TBq ^{137}Cs source. This radionuclide disintegrates in $^{137\text{m}}\text{Ba}$, which delivers 661.7 keV γ -Ray. A dose cartography has been performed by Fricke dosimetry inside the γ -Ray chamber and the average deposited dose inside the aqueous samples ranges from 7 to 9 Gy min^{-1} . As γ -Ray is a penetrating radiation, the dose is displayed almost equally everywhere inside the sample.

3.3. Radiolytic yield calculation

The radiolytic yield (G) is defined as the number of species formed or consumed per unit of deposited energy. It is expressed in the international system by mol J^{-1} and is calculated at a time t after transition of the ionizing irradiation according to:

$$G(X) = \frac{X_t}{\rho D} \quad (14)$$

where X_t is the concentration of the species X at the time t (mol L^{-1}), ρ is the density of the irradiated solution (kg L^{-1}) and D the absorbed dose (in Gy; $1 \text{ Gy} = 1 \text{ J kg}^{-1}$ of water).

The radiolytic yield is actually used to compare different systems and follow the species behavior (*i.e.* the production/degradation steps). A positive yield means that the species is formed during the irradiation. A negative one means that the species is consumed.

4. Dissolved carbonates degradation mechanism and carboxylates production yields

In the following sections, we document every step of dissolved carbonate degradation under irradiation. In this aim, radiolytic yields of production/degradation are measured for each involved species according to the following radiolytic process:

4.1. Carbonate anions behavior (Step I)

In a previous study (Costagliola et al. 2017), we have investigated the γ radiolytic degradation of a 1 mmol L⁻¹ calcium carbonate solution as the function of the accumulated dose up to 60 kGy. The carbonate degradation yield ($G_{\gamma}(-\text{CO}_3^{2-}) = 0.014 \mu\text{mol J}^{-1}$) was measured at low dose range (0 to 1000 Gy) under γ -Ray, thus under low LET. Here, the carbonate degradation was investigated under α -beam irradiation in order to determine the G-value which can be assigned to the high LET irradiation (#He-Carb experiment in **Table 1**).

Figure 1A, shows that the carbonate anions concentration first decreases ($G_{\alpha}(-\text{CO}_3^{2-}) = 0.079 \mu\text{mol J}^{-1}$) at low applied dose and further re-increases at higher dose ($G_{\alpha}(+\text{CO}_3^{2-}) = 0.011 \mu\text{mol J}^{-1}$). The corresponding production of formate, acetate and oxalate during dissolved carbonate α -beam irradiation is displayed on **Figure 1B**. The concentration of oxalate increases linearly with the cumulated dose within the 900 to 6000 Gy range ($G_{\alpha}(+\text{C}_2\text{O}_4^{2-}) = 1.0 \text{ nmol J}^{-1}$, $R^2 = 0.97$), but both formate and acetate exhibit a steady state concentration above 2000 Gy. Such a behavior remains valid up to 60 kGy, as observed by Costagliola et al. 2017. The back-formation of carbonate at high dose and the surprising behavior of the carboxylate byproducts is further discussed below.

Figure 1. A) carbonate, and B) carboxylate anions behavior during α -beam irradiation of a 0.2 mmol L⁻¹ carbonate-bearing solution (#He-Carb, Table 1). Experimental conditions: $E_\alpha = 60.7$ MeV, Dose Rate = 700-800 Gy min⁻¹, Ar atmosphere, pH = 10.

4.2. Formate Behavior (Step II)

Formate is the first species produced from the radiolytic degradation of carbonate anions as described in the literature (Costagliola et al. 2017). However, formate is unstable under irradiation and produces other carboxylate anions such as acetate and oxalate. That is the reason why formate stability was extensively studied during this work as a function of different parameters: formate initial concentration, LET effect, and gas production (H₂, CO₂).

First, the back-formation of carbonate associated to reaction step I (carbonate/formate anions mechanism) was demonstrated through the #He-High-Form experiment (**Fig. 2, Table 1**). Indeed, carbonates are produced ($G_\alpha(+CO_3^{2-}) = 0.098 \mu\text{mol J}^{-1}$) when a formate-bearing solution is irradiated using α -beam. This latter observation is crucial for understanding the back-formation of carbonate during step I (**Fig. 1A**). In the same dose range (0-1000 Gy), the comparison between G_γ ($-0.014 \mu\text{mol J}^{-1}$) and G_α ($-0.079 \mu\text{mol J}^{-1}$) for carbonate anions degradation confirmed the critical effect of LET on the enhancement of the radical/radical reactions. Indeed, α -beam irradiation favors radical/radical reactions (**Eqs. 6 to 8**) whereas γ -Ray irradiation promotes radical/molecular reactions (**Eqs. 1 to 5**) (Allen 1961). Therefore, the regeneration of carbonate from formate anion radiolysis is triggered by the recombination of radical species such as $CO_3^{\bullet-}$ and $CO_2^{\bullet-}$ (**Eqs. 7 to 13**).

Figure 2. Carbonate ion production from α -beam irradiation of a 1 mmol L⁻¹ formate-bearing solution (#He-High-Form, Table 1). Experimental conditions: $E_{\alpha} = 60.7$ MeV, DR = 700-800 Gy min⁻¹, aerated atmosphere, pH = 7.

Second, the behavior of formate anions under irradiation was studied as a function of both the LET (between 0.23 and 22.7 keV μm^{-1} for γ -Ray and α -beam, respectively) and the initial concentration in order to establish radiolytic degradation yield for this species. At the low formate concentration (0.01 mmol L⁻¹), the same degradation scheme is observed under both γ -Ray and α -beam irradiation (see **Fig. 2 and supplementary Figure S2**). Acetate is produced first, then oxalate appears (**Fig. 3A**). However, the formate degradation yield has been calculated at $G_{\alpha}(-\text{HCOO}^-) = 1.4$ nmol J⁻¹ and $G_{\gamma}(-\text{HCOO}^-) = 7.6$ nmol J⁻¹, which implies a strong dependency upon the radical mechanisms as already underlined (**Eqs. 9 to 13**). The acetate radiolytic production yield is about the same as the formate degradation one: $G_{\alpha}(+\text{CH}_3\text{COO}^-) = 1.6$ nmol J⁻¹. Thus, there is for low doses a quantitative transformation of formate to acetate. However, oxalate needs an induction period and starts to accumulate at elevated dose (>2000 Gy). The corresponding yield is then $G_{\alpha}(+\text{C}_2\text{O}_4^{2-}) = 0.6$ nmol J⁻¹.

At higher initial concentration (1 mmol L^{-1}), formate radiolysis seems to yield only oxalate (**Fig. 3B**). Probably, acetate remains at a very low concentration compared to formate as it is only an intermediate species between formate and oxalate. The formate consumption yield is by two orders of magnitude higher than in the low-formate concentration medium ($G_{\alpha}(-\text{HCOO}^{-}) = 0.130 \mu\text{mol J}^{-1}$). This is basically due to a kinetic effect from the concentration factor. The oxalate yield is here equal to $G_{\alpha}(+\text{C}_2\text{O}_4^{2-}) = 0.022 \mu\text{mol J}^{-1}$. Carbonate regeneration from formate irradiation, as previously described, is the main factor explaining such a low oxalate yield at high initial formate concentration.

Figure 3. Analysis of the carboxylate ions behavior as a function of α -beam irradiation dose for: A) a 0.01 mmol L^{-1} formate-bearing solution (#He-Low-Form, Table 1), and B) a 1 mmol L^{-1} formate-bearing solution (#He-High-Form, Table 1). Experimental conditions: $E_{\alpha} = 60.7 \text{ MeV}$, $\text{DR} = 700\text{-}800 \text{ Gy min}^{-1}$, aerated atmosphere, $\text{pH} = 7$.

Third, H_2 production during formate, acetate and oxalate degradation was monitored with increasing γ dose (**Fig. 4**, and **Table 2**). Molecular hydrogen formation by water radiolysis can be explained by the presence of aqueous electrons produced just after irradiation (about μs lifetime). These species react with each other to produce H_2 according to:

However, the Allen chain mechanism, *i.e.* the recycling of H_2 by $OH^\bullet$, keeps H_2 production under control (**Eqs. 16 and 17**). The corresponding H_2 radiolytic yield in pure water is then $0.017 \mu\text{mol J}^{-1}$ (**Fig. 4**).

In the presence of formate, this yield goes up to $0.11 \mu\text{mol J}^{-1}$. This is due to the fact that hydroxyl radical $OH^\bullet$ is efficiently scavenged by formate ((**10**), which limits the H_2 consumption by $OH^\bullet$ (**Eq. 16**). Moreover, the kinetic constant of $OH^\bullet$ scavenging by formate ions (**Eq. 10**) is approximately 100 times higher than the one by H_2 (**Eq. 16**). This enhanced H_2 production can be also explained by the scavenging of aqueous electron by formate itself ((**12**). Both the aqueous electron and the hydroxyl radical $OH^\bullet$ scavenging by formate have similar kinetic constants (**Eqs. 12 and 16**, respectively). Thus, at constant dose, H_2 production will be enhanced in the presence of formate because only one aqueous electron is needed instead of two.

Finally, CO_2 is also produced from the irradiation of formate solutions. It is the consequence of the reaction between formate and the water radiolysis radicals which forms $CO_2^{\bullet-}$ radicals. These radicals are efficiently scavenged by O_2 and, in a lesser extent, H_2O_2 to produce CO_2 according to:

The initial presence of dissolved O_2 is not a prerequisite for formate scavenging as water radiolysis itself provides an insitu source of oxidizing species (chiefly H_2O_2 and in a lesser extent O_2). Thus, in deep geological settings, the formate radical may be scavenged by H_2O_2 produced by water radiolysis (Eq. 19). Hydrogen peroxide was also monitored but no evidence of its

radiolytic production by γ -Ray of formate, acetate and oxalate solutions has been found. This is a direct consequence of the $\text{OH}^\bullet$ scavenging by carboxylates species as the H_2O_2 radiolytic formation mechanism is based on $\text{OH}^\bullet$ radical recombination (**Eqs. 9 and 10**).

Figure 4. Molecular hydrogen radiolytic production after γ -Ray irradiation of pure water (#G-water, losanges, Table 1), a 0.01 mmol L⁻¹ acetate-bearing solution (#G-Ac, squares, Table 1), and a 1 mmol L⁻¹ K₂CO₃ solution (Costagliola et al. 2017, triangles). Experimental condition: $E_\gamma = 0.6617$ MeV, DR = 7-9 Gy min⁻¹, aerated atmosphere, pH = 7.

Table 2. Molecular hydrogen ($G_\gamma(+\text{H}_2)$) and carbon dioxide ($G_\gamma(+\text{CO}_2)$) radiolytic γ yields.

*Data from Costagliola et al. 2017.

System composition	$G_\gamma(+\text{H}_2)$ $\mu\text{mol J}^{-1}$	$G_\gamma(+\text{CO}_2)$ nmol J ⁻¹
Water	0.017	0
Carbonate*	0.033	3.0
Formate	0.110	7.6
Acetate	0.037	7.0
Oxalate	0.014	12.0

In conclusion, the formate degradation mechanism follows two different paths: the first one consists in oxalate formation via acetate intermediate and radical recombination; whereas the second one results in carbonate formation with a non-negligible yield. Oxalate production is thus controlled by the first step of formate consumption.

4.3. Acetate/Oxalate Anions Behavior (Step III)

The same experiments, as for formate solution, were performed on the samples #G-Ac and #G-Ox (**Table 1**) in order to describe the behavior of acetate and oxalate under γ -Ray. When exposed to γ -Ray, acetate behaves very differently to formate. Here, oxalate can accumulate as acetate is degraded during the irradiation (**Fig. 5**). One can determine the $G_{\gamma}(-CH_3COO^-) = 9.4$ nmol J⁻¹ and the $G_{\gamma}(+C_2O_4^{2-}) = 7.7$ nmol J⁻¹ during this experiment.

Figure 5. Analysis of the carboxylate ions composition from γ -Ray of a 0.01 mmol L⁻¹ acetate-bearing solution (#G-Ac, Table 1). Experimental conditions: $E_{\gamma} = 0.6617$ MeV, DR = 7-9 Gy min⁻¹, aerated atmosphere, pH = 7.

Similarly, α -beam irradiation experiment has been carried out on both 0.01 and 1 mmol L⁻¹ acetate-bearing solutions (#He-High-Ac and #He-Low-Ac, respectively, **Table 1**) (**Fig. 6 and**

supplementary Figure S2). At low initial concentration, acetate is degraded by the ionizing radiations leading to oxalate formation which seems to reach a steady-state at elevated dose. Acetate is more stable than formate because its radiolytic consumption yield is more than three times lower than the one of formate ($G_{\alpha}(-\text{CH}_3\text{COO}^-) = 0.4 \text{ nmol J}^{-1}$). The formate anion formation observed at low dose is followed by a degradation process at elevated dose due to reaction between $\text{CO}_2^{\cdot-}$ and e_{aq}^- (Eq. 8). At high initial concentration acetate is not degraded into oxalate during the irradiation. However, the radiolytic consumption yield of acetate remains in good agreement ($G_{\alpha}(-\text{CH}_3\text{COO}^-) = 0.049 \text{ } \mu\text{mol J}^{-1}$) with the one measured at 0.01 mmol L^{-1} . From a carbon mass balance point of view, it can be noticed that up to 50 mol% of carbon cannot be assigned to the dissolved carboxylate anions quantified in this work. This is particularly evident at high formate or acetate initial concentration (Fig. 3B and 6B). An important part of this discrepancy may be explained by CO_2 degassing (as measured in part 4.2), but minor hydrocarbons (methane, ethane), organic polymers, and formaldehyde may also be produced (Draganić et al. 1991). Methane, however, has not been detected in these experiments (detection limit = 5 ppm), and the other species were not analyzed.

Figure 6. Analysis of the carboxylate ions composition from α -beam irradiation of: A) a 0.01 mmol L^{-1} acetate-bearing solution (#He-High-Ac, Table 1), and B) a 1 mmol L^{-1} acetate bearing

solution (#He-Low-Ac, Table 1). Experimental conditions $E_\alpha = 60.7$ MeV, DR = 700-800 Gy min^{-1} , aerated atmosphere, pH = 7.

The comparison of acetate degradation at low concentration (0.01 mmol L^{-1}) under either α -beam or γ -Ray (**Figs. 5 and 6A**, respectively), reveals a major effect of LET. Indeed, under γ -Ray, acetate is fully degraded into oxalate at a relatively low dose (1600 Gy), whereas only 50% of acetate is degraded into oxalate and minor formate at elevated α -beam irradiation dose (10500 Gy). Thus, the radiolytic degradation of acetate anions at low concentration (0.01 mmol L^{-1}) seems to mainly occur through radical reactions. These latter processes compete with the formate radical/radical reactions which produce oxalate anions (**Eq. 6**). However, these radical recombinations at play during acetate irradiation imply a lower H_2 production compare to the one measured with formate (see part 4.2). At high (1 mmol L^{-1}) acetate concentration, either the acetate anion itself scavenges all the formate radical or both acetate and formate react together to produce a more complex unidentified molecule.

Finally, concerning the results of the oxalate anions behavior under both α -beam and γ -Ray irradiations (#He-High-Ox, #He-low-Ox, and #G-Ox; **Table 1**) no change in concentration is observed for a large range of dose (up to 40 kGy) whatever both the radiation and the initial oxalate concentration within the $0.01 - 1 \text{ mmol L}^{-1}$ oxalate concentration range.

4.4. Summary of Yields-G

As a summary, **Table 3** compiles the different radiolytic yields of species consumption and formation due to both α -beam and γ -Ray irradiations, as determined in this study.

Table 3. Summary of the radiolytic yields of carbonate, formate, acetate and oxalate production/degradation due to both α -beam and γ -Ray irradiations as determined from the experiments performed in this work. * Data from Cai et al. (2001). *bdl* = below detection limit

Irradiated medium	Concent. (mmol L ⁻¹)	Yields G _{α} (nmol J ⁻¹)			Yields G _{γ} (nmol J ⁻¹)		
		Formate	Acetate	Oxalate	Formate	Acetate	Oxalate
Carbonate	0.2	0.4 ± 0.2	1.7 ± 0.9	1.0 ± 0.1			2*
Formate	0.01	- 1.4	1.6	0.59	- 7.6	<i>bdl</i>	<i>bdl</i>
	1	- 130	0	22			
Acetate	0.01	0.48	- 0.36	0.84	- 9.4	<i>bdl</i>	7.7
	1	0	-49	0			
Oxalate	0.01	0	0	0	0	0	0
	1	0	0	0			

Among the radiolytic yields reported in **Table 3**, only those concerning oxalate production can be applied over a large dose range, i.e. at least from 0 to 60 kGy. All the other yields are valid at low dose (typically 0 to 2000 Gy). This is because acetate and formate are intermediate species during carbonate degradation to oxalate.

From a geological perspective, and based on the detail understanding of the carbonate degradation mechanism presented here, we propose to use the oxalate production yield as a way to infer the carboxylate anions concentration in long residence time groundwaters where the cumulated dose can be very high. The oxalate production yield from carbonate irradiation is weakly affected by the LET compare to the other species. The G-value for oxalate production reported here under α -beam irradiation is 1 nmol J⁻¹, whereas Cai et al. 2001 indicate a G-value

of 2 nmol J⁻¹ under γ-Ray. Once oxalate concentration is known, one can derive the steady state concentration of formate and acetate depending on the dose and the initial concentration of carbonate. Under alkaline condition, it is interesting to note that the steady state concentration of formate and acetate seems to decrease when carbonate concentration increases. In this study, at a 0.2 mmol L⁻¹ carbonate concentration, and for α dose > 2000 Gy, the steady state concentrations of formate and acetate are at 1.8 and 7.0 μmol L⁻¹, respectively. Under the same irradiation condition, but at a five-time higher carbonate concentration (1 mmol L⁻¹), Costagliola et al. 2017 report a steady state formate and acetate concentration of 1.2 and 3.5 μmol L⁻¹, respectively. Cai et al. 2001 did not succeed to detect formate and acetate (detection limit = 1 μmol L⁻¹) after γ-Ray irradiation of a 50 mmol L⁻¹ carbonate-bearing solution.

5. Estimation of radiolytic carboxylate anions production in natural settings

In a given geological setting, the radiolytic oxalate production yield determined in this study ($G_{\alpha(+C_2O_4^{2-})} = 1 \text{ nmol J}^{-1}$), combined with the respective natural doses from α-, β-, and γ-radiations can be used to calculate the radiation-induced oxalate production rate from carbonate degradation. Several examples are displayed in **Table 4** for different subsurface environments with contrasted concentration of radioactive elements including Cigar Lake U-ore deposits (Canada), carbon leaders in the Witwatersrand basin (South Africa), granites in the Fennoscandian shield (Eurojoki Rapakivi, Finland), basalts in the Columbia River Basalt province, quartzites in the Witwatersrand Supergroup (South Africa), and sediments in the Taylorsville basin (Virginia, USA). Radiation doses have been computed by Truche et al. 2018 for Cigar Lake U-ore deposit, and by Lin et al. 2005 for the other settings.

The radiolytic oxalate production rate ranges from 10^{-10} to 10^{-5} nM s⁻¹ (**Table 4**) and depends chiefly on the radioactive elements content of the rock. Porosity in itself has only a minor impact on the oxalate production rates as most of the radiation energy (i.e. >99%) is dissipated in the solids and not absorbed by pore water (Truche et al. 2018). The obtained oxalate production rates are about 50 time lower than the radiolytic H₂ production rate reported by Lin et al. 2005 and Truche et al. 2018 for these geological environments, but they remain sufficiently high to sustain significant oxalate concentration in long residence time groundwaters. Without surprise, the Cigar Lake U deposit has the highest oxalate production rate (5.2×10^{-6} nM s⁻¹ = 0.16 M Myr⁻¹). Such a rate, together with a residence time of groundwater in the deposit of 0.1 Ma (Cramer and Smellie 1994), would imply a radiation-induced oxalate concentration as high as 16 mM. The groundwater in the Witwatersrand Supergroup has the lowest oxalate production rate (1.2×10^{-10} nM s⁻¹ = 3.8 μM Myr⁻¹), but its subsurface residence time spans from 3 to 80 Ma (Lippmann et al. 2003), which for these groundwater ages translates into 10 μM to 0.3 mM oxalate concentration. Whatever the context, the steady state concentration of formate and acetate produced would range from 1 to 10 μM.

Our estimates suggest that radiolysis can produce millimolar concentration of oxalate and micromolar levels of formate and acetate in ancient water from deep crystalline bedrocks if there is no biological or abiotic consumption. Such a reaction process does not require specific catalyst or hydrothermal condition to occur. The continuous production of carboxylate species from radiolytic origin, and their weak mobility compare to H₂, may promote their persistence in deep groundwater.

Another important consequence of carbonate radiolysis lies in an enhanced H₂ production compared to pure water radiolysis. Dissolved carbonates are ubiquitous in natural geological

settings, and H₂ production is probably much more important than previously anticipated on the basis of H₂ yield derived from carbonate-free solutions. Here, we demonstrate that H₂ production from dissolved carbonate radiolysis is enhanced by a factor 2 compare to pure water (**Table 2**).

Table 4. Radiolytic oxalate yield rates in various natural settings. Calculations for the net dose rates are from Lin et al. 2005 and Truche et al. 2018.

Rock type (location)	Porosity (%)	U (ppm)	Th (ppm)	K (%)	α -dose rate (Gy s ⁻¹)	β -dose rate (Gy s ⁻¹)	γ -dose rate (Gy s ⁻¹)	Oxalate rate (nM s ⁻¹)
U-ore deposit (Cigar Lake)	10	140,000	nd	nd	1.01×10^{-6}	3.23×10^{-6}	9.67×10^{-7}	5.21×10^{-6}
Carbon leaders (Witwatersrand basin)	0.1	40,000	8000	1	4.3×10^{-6}	2.4×10^{-11}	5.0×10^{-8}	4.31×10^{-6}
Granite (Fennoscandian Shield)	0.1	10	30	5.0	1.7×10^{-9}	1.2×10^{-10}	6.8×10^{-11}	1.89×10^{-9}
Basalts (Columbia River)	0.1	1	3	0.8	1.7×10^{-10}	1.9×10^{-11}	9.7×10^{-12}	1.90×10^{-10}
Quartzites (Witwatersrand Supergroup)	0.1	2	11	2	4.9×10^{-11}	4.6×10^{-11}	2.4×10^{-11}	1.19×10^{-10}
Sediments (Taylorsville Basin)	0.1	5	15	2.5	8.7×10^{-10}	6.5×10^{-11}	3.4×10^{-11}	9.69×10^{-10}

6. Implication for abiotic synthesis of organic compounds in geological settings

Carbonate radiolysis chiefly produces oxalate and leads to a boost of H₂ generation compare to pure water radiolysis. These two compounds are excellent energy sources, which can be oxidized by anaerobic microorganisms with nitrate, ferric iron, sulfate, or carbon dioxide as electron acceptors. Traditional perception of the metabolism of deep-dwelling microbes is that they are chemolithoautotrophic using inorganic carbon and H₂ as their energy source (Chapelle et al. 2002, Lin et al. 2005, Nealson et al. 2005). However, there is increasing evidence that organic acids sustained bacteria play a quantitatively important role in biological organic carbon cycling

424 in the marine and terrestrial deep biosphere (Heuer et al. 2009, Lever et al. 2010, Weiss et al.
425 2016; Pisapia et al. 2017). Among all the acetogenic substrates, oxalate oxidation can produce
426 energy yields exceeding the thermodynamic threshold concentration for growth and replication
427 in the deep subsurface (Lever 2012).

428 Bacteria capable of using oxalate as a sole carbon and energy source have been recognized as an
429 important part of the biogeochemical carbon cycle (Sahin 2003). More than 50 species of
430 oxalotrophic bacteria have been identified to date, some of these bacteria are generalists because
431 they are able to ferment many other substrates, but some others are “specialists” because they
432 only use oxalate as energy source, like *clostridium thermoaceticum* (Daniel and Drake 1993). In
433 addition, oxalate can also be used by fermenters that form formates and bicarbonates. If
434 ecosystems are present, some feedback loops are possible. Although fermentation is not as
435 energetically favorable as respiration, such a process does not need any electron acceptors, which
436 can be an advantage in reduced environments such as ancient cratons.

437 Primordial life, as inferred back from modern genomes, is depicted as a strictly anaerobic, H₂-
438 dependent thermophilic, diazotrophic autotroph with an Acetyl-CoA pathway and living in a
439 hydrothermal vent setting (Weiss et al. 2016). These are attributes of clostridia acetogens
440 lineages that branch deeply in trees of the last universal common ancestor genes and that occupy
441 the Earth’s crust today.

442 This cannot hide the fact that actual concentration of oxalate has not been measured in deep
443 crustal fluids, however. Only H₂, formate, and acetate concentration data have been published for
444 the deep subsurface biosphere (e.g. Sherwood Lollar et al. 2021). If some recent studies have
445 documented trace amounts of long chain monocarboxylic acids (propionate, butanoate,
446 pentanoate, hexanoate, and lactate), the presence of dicarboxylic acids, like oxalate, has never

447 been reported in deep fracture waters (Kieft et al. 2018, Onstott et al. 2009). This later species
448 may be microbiologically consumed or may have been overlooked as the total dissolved organic
449 carbon content measured in these environments is systematically higher to the combined
450 concentration of all dissolved organic species taken individually, indicating the presence of
451 substantial amounts of unclassified organic species. Oxalate is frequently reported in deep
452 sedimentary brines (Giordano and Kharaka 1994) and paleofluids entrapped in minerals (Zeng et
453 al. 2002), even if it represents a minor component of all the dissolved carboxylate anions
454 measured in formation waters. However, among all the carboxylic acids, oxalate displays some
455 unique properties that may explain its low concentration in deep crustal fluids. First, it is much
456 more unstable under hydrothermal condition than acetate or formate. At 80°C, oxalate half-life
457 ranges from 2500 to 28,000 years at pH values of 5 and 7, respectively (Crossey 1991). Aqueous
458 complexation decreases significantly (2 to 3 order of magnitude) the decarboxylation rate of
459 oxalate (Fein et al. 1994), but does not change the relative stability of carboxylate species under
460 prevailing hydrothermal conditions. Second, oxalate has a strong affinity for mineral surfaces
461 and it is known to catalyze mineral dissolution (Cama and Ganor 2006, Cheah et al. 2003, Mast
462 and Drever 1987). Adsorption at the surface of silicates and oxy-hydroxides may efficiently
463 decrease oxalate concentration in solution. Third, it is the only organic acid that naturally forms
464 solid phases such as whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) (Hofmann and
465 Bernasconi 1998). These Ca oxalate minerals are poorly soluble in circumneutral-alkaline
466 aqueous solution (Streit et al. 1998) and their existence has been documented in a wide variety of
467 diagenetic and hydrothermal environments and even in meteorites (Fuchs et al. 1973, Pizzarello
468 and Garvie 2014). The presence of oxalate in hydrothermal environments constitute clear
469 evidence that oxalic acid was an important constituent of many paleofluids (Hofmann and

Bernasconi 1998). Interestingly, oxalate-bearing phases are frequently associated with uraninite. An origin of oxalate as a result of radiolysis has been postulated based on field and laboratory evidence (Hasselstrom and Henry 1956; Hofmann and Bernasconi 1998). Thus, minerals may be an overlooked reservoir of oxalate in deep geological environments. In addition, oxalate can be consumed by fermenters that form formates and bicarbonates. Oxalate concentrations have either not been reported and are below detection limits to date for most fracture fluids studied in deep crystalline bedrock. This study suggests that oxalate should be a priority target analyte for future studies in these environments.

Carbonate radiolysis provide a consistent pathway for both enhancing the radiolytic H₂ production and generating carboxylic species potentially available for microbes. Accordingly, life in deep groundwater environments may not be solely supported by H₂ derived from abiotic water-rock interactions or by CH₄ and short-chain organic acids generated from geogenic H₂ via Fischer-Tropsch-type synthesis (Ménez 2020, Reeves and Fiebig 2020). This finding has also interesting implication for prebiotic chemistry and the development of life on other planets. In an extraterrestrial context, radiolysis has been considered as an H₂ production mechanism on Mars (Tarnas et al. 2018), Enceladus (Waite et al. 2017) and Europa (Bouquet et al. 2017). In addition to H₂, it is now interesting to consider the radiolytic production of carboxylate anions as key chemical components to support a subsurface biosphere. It has been suggested that salts of oxalic acids should be present in the Martian regolith, as they would be the primary end-products of meteoritic organic matter oxidative decomposition (Applin et al. 2015). We argue here that carbonate radiolysis can be an endogenous source of oxalate on Mars and other planetary bodies.

7. Conclusion

Radiation-induced carbonate degradation leads to both a boost of radiolytic H₂ production and the formation of carboxylate anions. At low dose, formate and acetate are favored whereas at higher dose oxalate is the most stable organic species. The carbonate radiolytic degradation follows a 3 steps reaction mechanism (Carbonate $\xrightarrow{I}$ Formate $\xrightarrow{II}$ Acetate $\xrightarrow{III}$ Oxalate).

(I) The formate anion formation is balanced by a re-production of carbonate due to formate degradation under α -beam irradiation.

(II) The formate breaks down the Allen chain by hydroxyl scavenging and increases drastically H₂ production. Formate radical is scavenged by dioxygen and produces carbon dioxide gas. Acetate is an intermediate species during the formate/oxalate degradation.

(III) Acetate degradation involves formate radical, and finally oxalate is strongly resistant under irradiation whatever the beam considered (α -beam or γ -Ray).

G-yields values of each carboxylate anions considered (formate/acetate/oxalate) are measured in low carbonate concentration solutions (0.01 to 1 mmol L⁻¹) exposed to α -beam or γ -Ray. These values together with the calculated dose rate and groundwater residence time allow the carboxylate anions concentration to be estimated in various deep geological settings. Irradiation-induced oxalate concentration may reach the millimolar range in deep ancient fracture fluids. This finding support the hypothesis that radiolytic carboxylates, with oxalate at the forefront, may contribute to fuel the deep subsurface lithotrophic microbial ecosystems as radiolytic H₂ does (Lin et al. 2005).

Carbonate radiolysis, may also produce other organic compounds such as formaldehyde and polymeric material (molecular weight: 14000-16000 daltons), this later being unidentified so far (Draganić et al. 1991). It is now of primary importance to reveal the yield and production mechanism of these organic species as they may also constitute an important part of the abiotic organic compounds available for the deep microbial ecosystems. Radiolysis is also known to be strongly affected by surface-mediated or catalytic reactions. The mechanisms and yields of carboxylate species measured here remain to be evaluated in the presence of minerals and particularly at the solid/solution interface where the specific surface area plays a major role in radiolytic gaseous species generation. Finally, the C, H isotopic signatures of carboxylate species produced experimentally during carbonate radiolysis and measured in deep fractured fluids have to be documented in order to improve the knowledge of their source.

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