

# Mineralogy and Sr–Mg geochemistry of charophyte carbonates: a new tool for paleolimnological research

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## Abstract

The carbonate biominerals formed in the oogonial cells and on stems of charophytes reveal intra-specific and species-to-species variations within the genus *Chara*. Calcite, high-magnesian calcite (HMC) and aragonite may be present in both oogonium and stem calcifications, and for the first time evidence is presented of polymineral calcification (HMC+aragonite) within single oogonial cells. The data indicate strong specific differences in the biological mechanisms of mineralization within this group of plants. Among the various species of the genus *Chara* studied, there is no correlation between the charophyte carbonate mineralogy and the salinity of water where they formed: calcite, HMC and aragonite may all be present in charophyte calcifications formed in low-salinity waters. On the contrary, there is an overall relationship between the mineralogy of these carbonates and the Mg/Ca ratio of the water in which they formed. Sr content in charophyte calcite and high Mg–calcite reflect directly the Sr/Ca ratio of the host water, whereas Mg content in these carbonates probably depends on the temperature and the Mg/Ca ratio of the water. Partitioning coefficients for Mg and Sr for some widespread species are discussed. Our results indicate that charophyte carbonates may be used as paleohydrochemical proxies and imply that special attention must be paid to the mineralogical control of charophyte carbonates when they are to be used in isotopic studies. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* aragonite; calcite; Charophyta; lacustrine features; paleolimnology

## 1. Introduction

Charophytes are aquatic, mostly freshwater green plants phylogenically related to early land plants (embryophytes). Some charophytes may

produce carbonate biominerals which constitute significant deposits in lakes [1]. The modes of charophyte biomineralization include biologically induced external encrustations on the cell walls of the stems [2] and organic-matrix-mediated calcification [3] within the walls of the spiral cells of the oogonium of some species. The oogonium is the integral structure in which the reproductive cell or oospore is completely ensheathed by spiral, vegetative cells [4]. The oogonium may also become encrusted with calcium carbonate [5]. This external carbonate deposit has similar fea-

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tures and origin to the stem encrustations. In our work, we have only dealt with the internal calcifications in oogonial spiral cells (i.e. within the cell wall) forming the mineralized layer called calcine. The carbonate remains of a calcified oogonium, which is able to fossilize, is called a gyrogonite.

Biom mineralization in oogonia and on stems is limited to certain charophyte groups; some species calcify regularly, several rarely, and some never. The external calcifications on stems constitute annular bands in some ecorticate species like *Chara corallina* or *Chara braunii* [6], or they form apparently non-banded encrustations on stems of some ecorticate and many corticate species [2] like *Chara vulgaris* or *Chara hispida*.

Although the cellular physiology has been intensively investigated for some ecorticate species of *Chara* (*C. corallina*, *C. braunii*) [7] and the photosynthetic uses of calcification have been also investigated [8], little attention has been paid to the mineralogy and chemistry of charophyte biom mineralization [9–11]. This is despite the fact that charophyte carbonates, especially the stem encrustations of *Chara*, are major components of sediments in some lakes [1]. The characterization of charophyte carbonate is of great importance because in recent years the stem encrustations from some *Chara* species have been used for  $\delta^{18}\text{O}$  investigations of continental climate [12,13] including, in some cases, the assumption that the charophyte carbonate is calcite without the need for any mineralogical control for isotope fractionation corrections (e.g. [14]). In fact, the  $\delta^{18}\text{O}$  values of calcite and high-magnesian calcite (HMC) must be corrected for the  $\text{MgCO}_3$  content [15], and  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of aragonite must be corrected due to the aragonite–calcite fractionation [15,16]. Additionally,  $\text{Mg}/\text{Ca}$  or  $\text{Sr}/\text{Ca}$  ratios in Ca–Mg carbonate biominerals are also increasingly being used as empirical paleothermometers, especially from foraminifers [17], corals [18] and ostracods [19]. Our study, which focused on the mineralogy of charophyte carbonates, and on the  $\text{Mg}/\text{Ca}$  and  $\text{Sr}/\text{Ca}$  ratios of the charophyte calcites and HMCs, offers promising perspectives for using some of the geochemical characteristics of these carbonates as

paleoenvironmental proxies for Pliocene and Quaternary lake records.

## 2. Materials and methods

The mineralogy of the charophyte carbonates was determined by standard X-ray powder diffraction (XRD) analyses performed with a Siemens D-500 X-ray diffractometer using  $\text{CuK}\alpha$  radiation. When very little sample was available (i.e. few gyrogonites), XRD patterns were obtained from a Debye–Scherrer geometry diffractometer (INEL CPS-120) with the powder microsample allocated within capillary tubes (0.2–0.3 mm of diameter).

Water analyses have been performed by inductively coupled-plasma-optic emission spectroscopy (ICP-OES) and other standard methods [20]. The Sr and Mg contents for monomineral charophytic calcite and HMC, expressed as  $\text{Sr}/\text{Ca}$  and  $\text{Mg}/\text{Ca}$  molar ratios, and mol%  $\text{MgCO}_3$  (Table 1), have been obtained by ICP-OES (Thermo Jarrell Ash) at the Serveis Científic-Tècnics (Universitat de Barcelona, Spain). Powder carbonate samples have been dissolved in dilute ultrapure  $\text{HNO}_3$  acid (2%). The solution was analyzed for Ca (317.933 nm), Mg (279.553 nm) and Sr (421.552 nm). Limits of detection are 0.025 ppm for Ca, 5 ppb for Mg and 5 ppb for Sr. All analyses were run against multi-element standards prepared from Johnson Matthey<sup>®</sup> stock solutions. The mean precision of the analyses was: 0.5% for Ca, 2.7% for Mg, and 0.6% for Sr.

A number of charophyte stem encrustations and some rare gyrogonites (calcified oogonia cells) are composed of two carbonate minerals (i.e. HMC and aragonite). The quantitative determinations of the mol%  $\text{MgCO}_3$  in calcites from these carbonates has been attempted through the precise position of the  $d_{104}$  obtained by XRD analyses [22]. However, the use of X-ray determinative curves based on synthetic phases like that from Goldsmith et al. [22] can lead to errors of over 5 mol%  $\text{MgCO}_3$  in the estimation of biogenic calcite [23]. We have constructed a graph for charophyte carbonates by considering mol%  $\text{MgCO}_3$  in charophyte calcite from  $d_{104}$  peak against mol%

Table 1  
Analytical data from waters and charophyte carbonates

Location	Environment	Sample number	Species	Water		Gyrogonites (calcified oogonia)				Stem encrustations					
				salinity	%	Sr/Ca <sub>mol</sub>	Mg/Ca <sub>mol</sub>	mineralogy	Sr/Ca <sub>mol</sub>	Mg/Ca <sub>mol</sub>	mol% MgCO <sub>3</sub>	mineralogy	Sr/Ca <sub>mol</sub>	Mg/Ca <sub>mol</sub>	mol% MgCO <sub>3</sub>
Montcortés-1, NE Spain	Spring pond	1	<i>Chara cf. vulgaris</i>	0.38	0.0005	0.05	0.0005	C	N.D.	0.0035	0.35	C	0.0002	0.0098	0.97
Balcón de Rioja, N Spain	Creek	2	<i>C. vulgaris</i>	0.50	0.0003	0.08	0.0003	not calcified	–	–	–	–	0.0002	0.0102	1
Montcortés-2, NE Spain	Spring pond	3	<i>C. vulgaris</i>	0.29	0.0010	0.14	0.0010	C	0.0002	0.0103	1.02	C	0.0004	0.0177	1.74
Arnedillo, N Spain	River (saline spring)	4	<i>C. vulgaris</i>	3.68	0.0092	0.31	0.0032	C	0.0032	0.0166	1.63	C	0.0029	0.0147	1.45
Montcortés-3, NE Spain	Lake sediment	5 <sup>s</sup>	<i>Chara sp. 1</i>	0.40	0.004	0.30	0.004	C	N.A.	N.A.	2.74 <sup>a</sup>	C	0.0012	0.0157	1.54
Montcortés - 3, NE Spain	Lake (margin a)	6	<i>C. vulgaris</i>	0.41	0.0040	0.31	0.0040	not calcified	–	–	–	C	0.0014	0.0172	1.69
Montcortés-3, NE Spain	Lake (margin b)	7	<i>C. vulgaris</i>	0.28	0.0046	0.40	0.0046	C	0.0015	0.0347	3.35	C	0.0015	0.0268	2.61
Bárceña, N Spain	Lake	8	<i>C. gr. vulgaris</i>	0.59	0.0079	0.36	0.0079	not calcified	–	–	–	C	0.0025	0.0194	1.9
Arreo, N Spain	Lake	9	<i>C. hispida</i>	1.08	0.0042	0.35	0.0042	C	0.0022	0.0357	3.45	C(+trA)	N.D.	N.D.	1.7 <sup>a</sup>
St. V. Barbeyragues, S France	Pond	10	<i>C. vulgaris</i>	0.18	0.0031	0.38	0.0031	C	0.0008	0.0295	2.86	C	0.0005	0.0122	1.2
Oree, S Spain	River	11	<i>Chara sp. 2</i>	0.75	0.0079	0.43	0.0079	C	0.0027	0.0246	2.40	C	0.0030	0.0235	2.29
Monast. de Piedra, N-C Spain	River lake	12	<i>C. hispida</i>	0.60	N.A.	0.43	0.0010	C	0.0010	0.0199	1.95	C(+trA)	N.D.	N.D.	3.15 <sup>a</sup>
Balsa de Chirprana, N Spain	Small pond	13	<i>Chara gr. globularis</i>	3.88	0.0097	0.69	0.0097	HMC	0.0055	0.0485	4.62	C	N.A.	N.A.	1.39 <sup>a</sup>
Lledó, N Spain	River	14	<i>Chara cf. hispida</i>	0.45	0.003	0.66	0.003	C	0.0012	0.0380	3.66	C(+A)	N.D.	N.D.	2.74 <sup>a</sup>
Centicero, N Spain	Spring pond	15	<i>C. vulgaris</i>	0.77	0.0128	1.16	0.0128	C	0.0038	0.0399	3.83	C	0.0045	0.0366	3.53
Tortajada, N-C Spain	Saline small lake	16	<i>C. hispida</i>	5.11	0.006	1.29	0.006	HMC	0.0055	0.0616	5.80	C(+A)	N.D.	N.D.	2.74 <sup>a</sup>
Calaceite, N-C Spain	Small pond (1999)	18	<i>C. globularis</i>	0.54	0.0145	0.88	0.0145	HMC	0.0087	0.1415	12.39	HMC	0.0103	0.0616	5.8
Calaceite, N-C Spain	Small pond (1997)	19	<i>C. globularis</i>	0.24	0.026	1.22	0.026	HMC	0.0139	0.1143	10.26	HMC+A	N.D.	N.D.	6.57 <sup>a</sup>
Calaceite, N-C Spain	Small pond (1998)	20	<i>C. globularis</i>	1.02	0.0504	3.44	0.0504	HMC(+A)	N.D.	N.D.	10.71 <sup>a</sup>	HMC(+A)	N.D.	N.D.	6.98 <sup>a</sup>
Torreblanca-1, E Spain	Brackish pond	21	<i>C. hispida</i>	5.72	0.0046	1.34	0.0046	HMC	0.0019	0.0678	6.35	HMC+A	N.D.	N.D.	5.01 <sup>a</sup>
Torreblanca-2, E Spain	Brackish pond	22	<i>C. hispida</i>	6.14	0.0039	1.33	0.0039	not calcified	–	–	–	HMC(+A)	N.D.	N.D.	4.5 <sup>a</sup>
Oso de Sió, N Spain	Small pond	23	<i>C. globularis</i>	6.30	0.0266	6.1	0.0266	A+HMC	N.D.	N.D.	24.38 <sup>a</sup>	A+HMC	N.D.	N.D.	11.75 <sup>a</sup>
Tanganyika, E Congo	Lake	24 <sup>s</sup>	<i>C. zeylanica</i>	0.41	0.0058	5.98	0.0058	HMC	0.0035	0.2411	19.42	A(+HMC)	N.D.	N.D.	19.83 <sup>a</sup>
Salada Chirprana, N Spain	Small saline lake	25 <sup>s</sup>	<i>Chara cf. galioides</i>	52.12	0.0180	17.8	0.0180	HMC	0.0048	0.3147	23.94	A(+HMC+tr)	N.D.	N.D.	N.D.
Salada Chirprana, N Spain	Small saline lake	26 <sup>s</sup>	<i>L. papulosum</i>	52.12	0.0180	17.8	0.0180	HMC	0.0071	0.4681	31.88	(this species does not produce stem encrustations)			

A, Aragonite; C, calcite; HMC, high-magnesian calcite; tr, traces. Monasterio de Piedra water data after C. Arenas (unpublished). Tanganyika water data by Bar-rat et al. [21]. N.A., not available; N.D., not determined because of the low amounts of the element (Sr) or of the mineral (HMC) in the sample, or because mixed mineralogy; mol% MgCO<sub>3</sub> in carbonate after Mg/Ca from ICP analyses (see Section 2)

<sup>a</sup> Samples where aragonite is present. In this case, mol% MgCO<sub>3</sub> calculated after XRD (see Section 2).

<sup>s</sup> Subrecent material from dead plants or sediment.

MgCO<sub>3</sub> in charophyte monomineral carbonate from molar Mg/Ca ratios obtained from ICP analyses using the following formula: mol% MgCO<sub>3</sub> = 100 × (Mg/Ca)/(1+(Mg/Ca)). For 29 paired analyses on monomineral samples,  $R^2 = 0.974$ ; [mol% MgCO<sub>3</sub>(ICP) = 1.391 + 1.037 (mol% MgCO<sub>3</sub> from XRD)],  $P = 1.3E-05$ . The results for estimations of mol% MgCO<sub>3</sub> in our charophyte calcites from XRD show a smaller deviation (standard error = 1.22) than those previously reported [23]. The mol% MgCO<sub>3</sub> calculated from ICP is about 1.4% higher than the mol% MgCO<sub>3</sub> estimated from XRD. Consequently, for the monomineral carbonates in this paper we have considered the mol% MgCO<sub>3</sub> in calcite and in HMC as the values calculated from molar Mg/Ca ratios obtained from ICP analyses. For the polymineral carbonates, mol% MgCO<sub>3</sub> in calcite and in HMC have been estimated from XRD patterns by application of our regression equation. In this case the above-mentioned inaccuracies must be taken into account.

### 3. Charophyte carbonate mineralogy

It has been widely assumed that charophyte carbonates are mostly composed of calcite, or HMC for the gyrogonites from some brackish water species [4], although a more varied mineralogy has been occasionally reported for stem encrustations formed in cultures [9], or for gyrogonites from diverse non-marine aquatic environments [10].

Our observations, from 20 non-marine aquatic environments with varied water chemistries and salinities, reveal for the first time significant mineralogical variations in both gyrogonite and stem calcifications (Table 1). In contrast with most biogenic carbonates, in which each individual taxon (species or higher taxonomic levels) usually displays a fixed mineralogy [24,25], our findings indicate: (1) individual species variation in the mineralogy of the carbonate biomineralizations within the genus *Chara* (i.e. *C. vulgaris* versus *Chara globularis*), and (2) intra-specific variations in the mineralogy of the carbonates produced by some taxa (i.e. in *C. globularis*). Gyrogonites were

composed of calcite or HMC with up to 23.9 mol% MgCO<sub>3</sub> in *Chara cf. galioides*, and 31.9 mol% MgCO<sub>3</sub> in *Lamprothamnium papulosum*. This is among the highest mol% MgCO<sub>3</sub> recorded for biogenic carbonates. To date, the highest MgCO<sub>3</sub> percentages in biogenic HMC (29–35 mol% MgCO<sub>3</sub>) have been reported from red algae [23,26,27]. Unusual mixtures of HMC and aragonite, as in some gyrogonites from *C. globularis* have been noticed. In the last case, our scanning electron microscopy–energy dispersive X-ray (SEM–EDX) observations (Fig. 1) show that HMC and aragonite are present in separate layers within individual cells of the gyrogonite. This is the first published evidence of polymineral calcification within single oogonial cells. The origin of this polymineral calcification may be related to the hydrochemical instability of the small pond where these *C. globularis* plants developed during the summer 1998, leading to changing conditions of diverse environmental parameters, significantly Mg/Ca<sub>water</sub> (Mg/Ca<sub>w</sub>), during the calcification period of the oogonia. Aragonite is rare in oogonia but much more common in stem encrustations which may be locally abundant and form aragonitic layers [28]. The mineralogy of stem encrustations varies from monomineralic (calcite, HMC or aragonite) to variable mixtures of calcite and aragonite, or HMC, and aragonite (Table 1). These features indicate more complicated structures and mineralogy than has previously been described for gyrogonites and for stem encrustations, and the need for further research on the formation and ultrastructural features of charophyte calcifications.

Contrary to the suggestions of other authors (reported in [4]), among the various species of the genus *Chara* studied here, no correlation exists between the charophyte carbonate mineralogy and the salinity of the water where they formed (Fig. 2a). The data clearly indicate that calcite, HMC and aragonite may all be present in charophyte calcifications formed in low-salinity waters. For example, *C. vulgaris* forms calcite gyrogonites and stem encrustations in low salinities (0.3–3.9‰ S), whereas *Chara zeylanica* in the fresh-water Lake Tanganyika (0.4‰ S) developed HMC gyrogonites (19.4 mol% MgCO<sub>3</sub>) and ara-

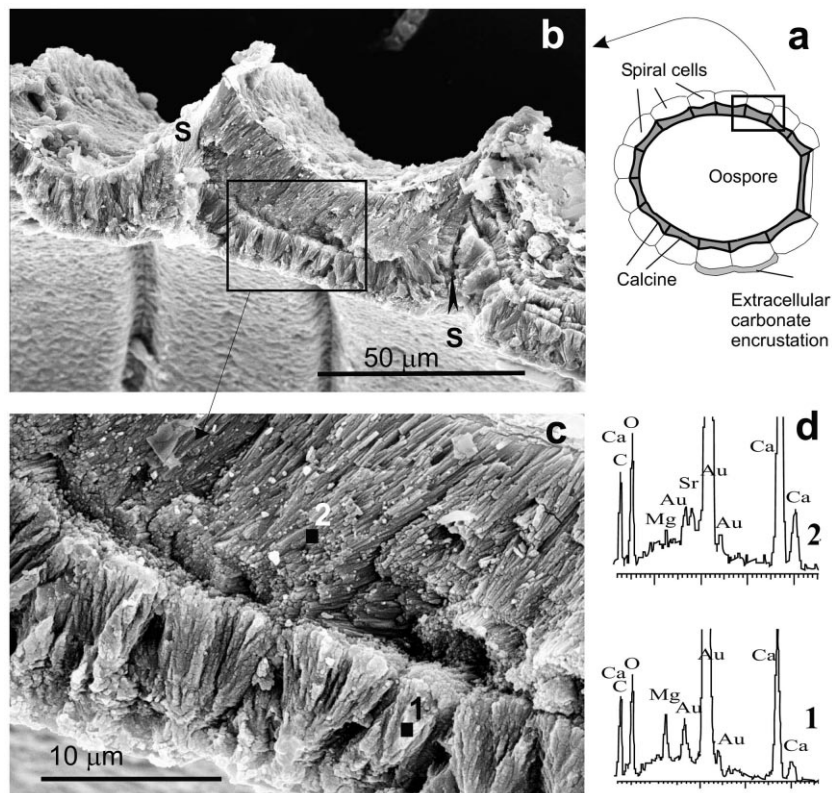


Fig. 1. Evidence for polymineral calcification within single oogonial cells of *C. globularis*, from Calaceite pond, north-central Spain (sample 20 in Table 1). (a) Sketch of a section of the oogonial spiral cells ensheathing the oospore. Deposition of calcite starts along the adaxial walls of the spiral cells forming the calcine, or calcified cell wall. Extracellular spiral cell deposits also may be formed. (b) Transverse SEM image of a section of the calcine, or calcified adaxial walls from three calcified spiral oogonial cells. The organic material from the spiral cells, including the abaxial cell walls, as well as the oospore have been removed. S indicates the suture between the calcine from two spiral cells, corresponding to the position of the adjacent cell walls. (c) SEM image of the selected area in the calcine of a single cell in (b). 1 and 2 indicate location of the energy dispersive X-ray (EDX) analyses. The calcine consists of two main layers: the inner layer (lower in the photograph) is formed by fan-shaped aggregates of HMC, whereas the outer layer (upper in the photograph) is formed by fibrous aragonite. (d) EDX spectra from the two calcine layers in (c). Spectrum 1, characterized by a significant Mg peak and absence of a Sr peak, corresponds to HMC (10.7 mol%  $\text{MgCO}_3$  after XRD). Spectrum 2, characterized by significant presence of Sr and low content of Mg, indicates aragonite. Both carbonate minerals have been identified by XRD analyses on powder from several calcified oogonia.

gonite stem encrustations. Some *Chara* species always produces the same biominerals (i.e. only calcite in *C. vulgaris*) whereas other taxa, like *C. globularis*, may form stem encrustations of calcite, HMC, or even aragonite and HMC within the same salinity range in which *C. vulgaris* mineralizes only calcite (Table 1 and Fig. 2). This indicates strong specific differences in the biological mechanisms of mineralization within this group of plants, in contrast to the apparently more ho-

mogeneous biomineralization behavior shown by species of red algae [24].

#### 4. Mg/Ca and Sr/Ca in charophyte Ca–Mg carbonates

In order to evaluate the potential application of Mg and Sr content in charophyte calcite and HMC for paleoenvironmental research, we have

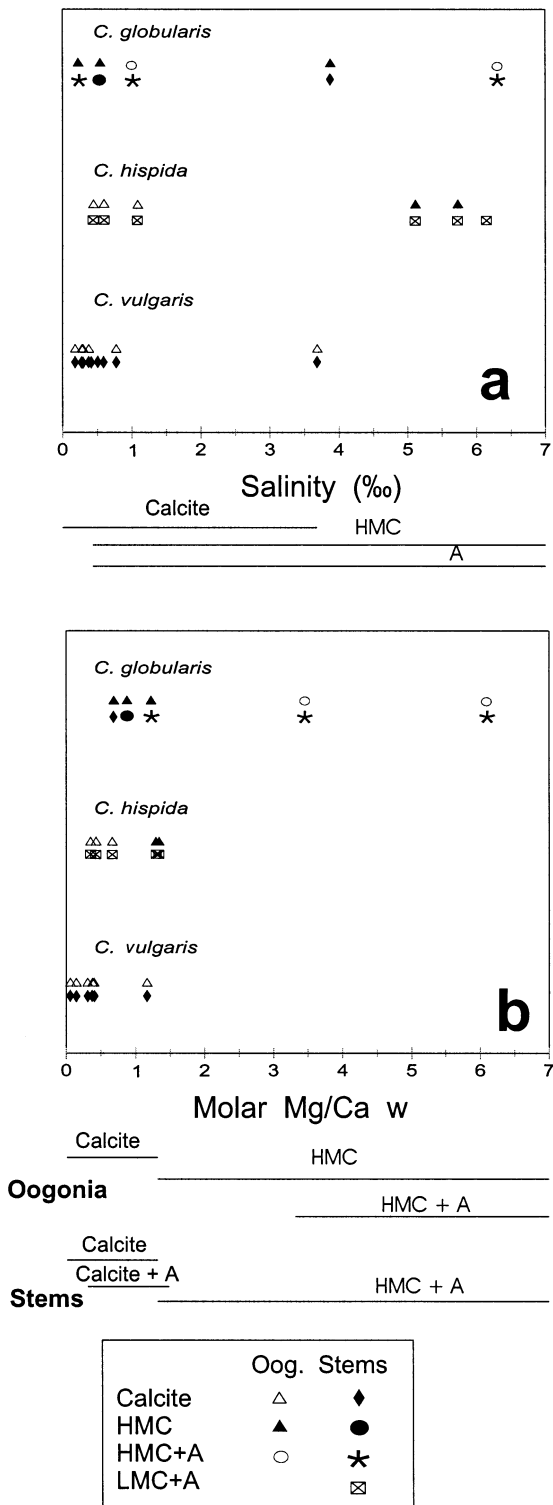


Fig. 2. Mineralogy of gyrogonites and stem encrustations from diverse charophyte species (a) versus ranges for salinity, and (b) versus Mg/Ca molar ratios from waters where they formed.

determined the Mg/Ca and Sr/Ca ratios in gyrogonites and stem encrustations, mostly from the same plants, for diverse charophyte species, and the corresponding cation ratios in the waters where they formed (Table 1). The Mg/Ca ratio in water is a primary determinant of the mineralogy of abiotic Ca–Mg carbonates precipitated in lacustrine environments [29]. Our results also indicate an overall relationship between Mg/Ca<sub>w</sub> and the mineralogy of the charophyte carbonates (Fig. 2b). Nevertheless, slight differences in mineralogy between the gyrogonites and the stem encrustations have been observed in some species like *C. hispida* or *C. galioides* (Table 1 and Fig. 2). Moreover, the diverse ranges of Mg/Ca<sub>w</sub> for mineral formation in charophyte carbonates shown in Fig. 2b differ from the ranges of Mg/Ca<sub>w</sub> in which the diverse Ca–Mg carbonates precipitate abiotically in lakes [29]. Although there are insufficient data for establishing if different biominerals are formed by different taxa growing in the same water, our observations indicate an overlap of the Mg/Ca<sub>w</sub> ranges in which some species produce encrustations with different mineralogies (Fig. 2b). For example *C. hispida* forms calcite stem encrustations with varying amounts of aragonite (from traces in sample 12 up to 15% in sample 14) at low Mg/Ca<sub>w</sub> and low salinity, whereas other taxa (e.g. *C. vulgaris*) apparently forms only calcite over similar Mg/Ca<sub>w</sub> and salinity ranges. These features point to a species-dependent Mg uptake behavior for some charophytes.

There is a close relationship between the Mg/Ca in calcite or HMC from gyrogonite and stem encrustations collected from the same plant ( $R^2 = 0.875$ ; for eight monomineral samples). The slope of the regression line [ $Mg/Ca_{gyrog} = -0.02 + 2.4 (Mg/Ca_{stem})$ ;  $P = 0.00034$ ] indicates that Mg uptake in gyrogonite calcite or HMC is significantly higher than in the respective stem carbonates. A combination of ICP and XRD nor-

malized data (see Section 2) allows us to consider a higher number of observations. In this case, the overall relationship between Mg content (expressed as mol%  $\text{MgCO}_3$ ) in gyrogonite and in stem carbonate, is enhanced [ $R^2 = 0.904$ ,  $n = 17$ ;  $P = 2.48\text{E-}09$ ]. The correlation between mol%  $\text{MgCO}_3$  in charophyte Ca–Mg carbonates and salinity is not significant [ $R^2 = 0.157$ ,  $n = 44$ ]. In fact, high-Mg content in charophyte HMC (mostly in gyrogonites) is attained at either high salinities (i.e. 24%  $\text{MgCO}_3$  in *C. galioides* grown at 52‰ S) or at low salinities (i.e. 19.4%  $\text{MgCO}_3$ , in *C. zeylanica* grown at 0.41‰ S;) (Fig. 2 and Table 1).

There is a significant correlation between  $\text{Mg}/\text{Ca}_w$  and  $\text{Mg}/\text{Ca}_{\text{calcite}}$ :  $R^2 = 0.822$ ,  $n = 30$ ;  $P = 6.74\text{E-}15$ . The slope (coefficient) of the regression equation [ $\text{Mg}/\text{Ca}_{\text{calcite}} = 0.0237 (\text{Mg}/\text{Ca}_w)$ ] provides an approximate estimation for the partition coefficient of Mg ( $K_d\text{Mg}$ ) between charophyte calcite and ambient water. This value is comparable to that reported by several authors for  $K_d\text{Mg}$  for abiotic calcites [30]. A lower, although significant overall correlation is attained for  $\text{Mg}/\text{Ca}_w$  and mol%  $\text{MgCO}_3$  in charophyte calcite from combined analyses (ICP and XRD) which include a higher number of data, particularly of calcite and HMC from polymineral samples ( $n = 44$ ;  $R^2 = 0.670$ ; coef. = 1.955;  $P = 2.76\text{E-}17$ ). If we consider separately the calcification of gyrogonites and stems, there is a significant correlation between  $\text{Mg}/\text{Ca}_w$  and  $\text{Mg}/\text{Ca}$  in gyrogonites [ $R^2 = 0.806$ ,  $n = 18$ ;  $\text{Mg}/\text{Ca}_{\text{gyrog}} = 0.0235 (\text{Mg}/\text{Ca}_w)$ ;  $P = 1.65\text{E-}09$ ], whereas this correlation is significantly lower for stems [ $R^2 = 0.543$ ;  $\text{Mg}/\text{Ca}_{\text{stem}} = 0.048 (\text{Mg}/\text{Ca}_w)$ ,  $n = 12$ ;  $P = 1.82\text{E-}06$ ]. Differences in slope for these correlation lines reveal different  $K_d\text{Mg}$  values for calcites from stem and gyrogonites. This is consistent with the differences in Mg contents in gyrogonite and stem from individual plants noted above. If individual species, like *C. vulgaris* or *C. hispida* (Fig. 3a), are considered, the correlation between  $\text{Mg}/\text{Ca}_w$  and  $\text{Mg}/\text{Ca}$  from the diverse Ca–Mg carbonates is lower than the corresponding values for overall data, although there is a significant correlation between  $\text{Mg}/\text{Ca}_w$  and  $\text{Mg}/\text{Ca}_{\text{gyrog}}$  for *C. hispida*. There is notable dispersion in the  $K_d\text{Mg}$  between

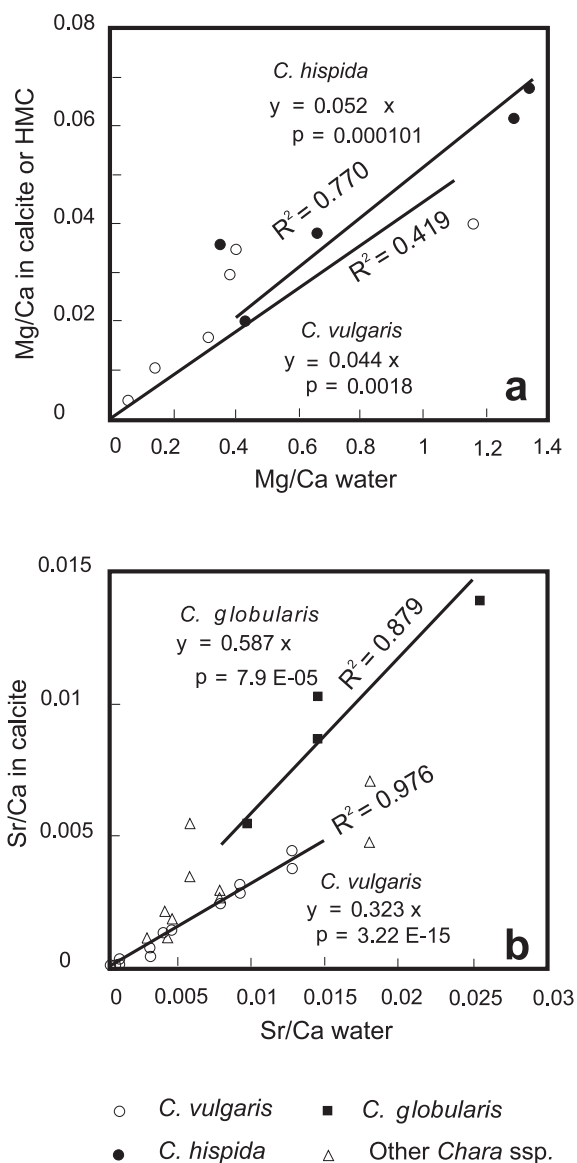


Fig. 3. (a) Molar Mg/Ca in gyrogonite calcite as a function of the water Mg/Ca for individual species. Data in Table 1. (b) Molar Sr/Ca in charophyte calcite as a function of the water Sr/Ca. Data in Table 1. Only regression lines for *C. globularis* and *C. vulgaris* are shown. For *C. vulgaris* similar high correlations and slopes exhibit separately gyrogonite, and stems: *C. vulgaris*<sub>oogon</sub>:  $R^2 = 0.979$  ( $n = 5$ ; slope 0.313; standard error = 0.013); *C. vulgaris*<sub>stems</sub>:  $R^2 = 0.976$  ( $n = 9$ ; slope 0.331; standard error = 0.012).

charophyte carbonate and water for *C. hispida* and for *C. vulgaris*, as may be deduced from the poor fit of the  $\text{Mg}/\text{Ca}_w\text{--Mg}/\text{Ca}_{\text{carbonate}}$  plot in Fig. 3a. Reaction rates seem not to influence the  $\text{Mg}^{2+}$  partitioning coefficient in calcite over the range of saturation states likely to be encountered in these natural systems [31], contrary to that argued by other authors [32]. Therefore, the  $K_d\text{Mg}$  dispersion probably reflects the effect of temperature on the uptake of  $\text{Mg}^{2+}$  in gyrogonites and stem encrustations, and the influence of  $\text{Mg}/\text{Ca}_w$  on calcite  $K_d\text{Mg}$  for low  $\text{Mg}/\text{Ca}_w$  values. Temperature changes usually induce changes in Mg uptake and therefore in  $K_d\text{Mg}$  in many biogenic carbonates [23,26]. Moreover, a relationship between  $K_d\text{Mg}$  and water  $\text{Mg}/\text{Ca}$  has been observed for abiotic calcite [33] and in some ostracod species [34]. In these cases, at very low water  $\text{Mg}/\text{Ca}$  ratio,  $K_d\text{Mg}$  increases with decreasing water  $\text{Mg}/\text{Ca}$ . A relationship of this type is obtained for *C. vulgaris* stem calcites at values of  $\text{Mg}/\text{Ca}_w$  lower than 0.4, although we have insufficient data to prove consistent relationships between  $K_d\text{Mg}$  in other charophyte calcites and water  $\text{Mg}/\text{Ca}$ . The different slope for each species in Fig. 3a probably reflects specific vital effects linked to one or both of these features.

Regardless of the different type of biomineralization process that operates on the walls of the stem cells and within the wall of the oogonium cells [2,4,35], there is a significant and strong correlation between the Sr/Ca ratios in gyrogonites and stem encrustations from the same plants [ $R^2 = 0.989$ ,  $n = 7$ ;  $\text{Sr}/\text{Ca}_{\text{gyrog}} = 0.0002 + 0.82 (\text{Sr}/\text{Ca}_{\text{stem}})$ ;  $P = 6.11\text{E-}07$ ]. Considering only *C. vulgaris* data, the high correlation is retained [ $R^2 = 0.950$ ;  $\text{Sr}/\text{Ca}_{\text{gyrog}} = 0.0002 + 0.86 (\text{Sr}/\text{Ca}_{\text{stem}})$ ,  $n = 5$ ;  $P = 0.00163$ ]. These notable correlations, and the slope value of the regression lines indicate similar Sr uptake features for gyrogonites and stem encrustations. In fact the slope of the regression line (0.82–0.86) indicates that Sr uptake is slightly lower in oogonia than in stems. A significant overall relationship exists between  $\text{Sr}/\text{Ca}_{\text{water}}$  and  $\text{Sr}/\text{Ca}_{\text{carbonate}}$  for all data, gyrogonite and stem encrustations ( $R^2 = 0.796$ ,  $n = 28$ ;  $P = 1.62\text{E-}15$ ) and some distinct regression lines may be distinguished (Fig. 3b). The correlation for *C. vulga-*

*ris* is significant ( $R^2 = 0.976$ ), and there are also strong correlations between Sr/Ca calcite and Sr/Ca water for gyrogonites and stems. The regression slopes provide approximate estimations for  $K_d\text{Sr}$  between charophyte calcite and ambient water. Two distinct mean  $K_d\text{Sr}$  values may be considered: about 0.323 for *C. vulgaris*, and about 0.59 for *C. globularis* carbonates. Therefore, our data suggest species-dependent Sr uptake for charophyte carbonates. Although *C. vulgaris* and *C. globularis* are included in the corticated subgenus *Chara*, they are not closely related species; *C. vulgaris* belongs to section *Chara* whereas *C. globularis* and related taxa belong to section *Grovesia* [36]. The estimated mean  $K_d\text{Sr}$  values for *C. vulgaris* are within the range 0.15–0.35 estimated for  $K_d\text{Sr}$  from most abiotic calcite overgrowths which have  $\text{MgCO}_3$  contents between 0 and  $> 10$  mol% [33]. Compared with biogenic calcites, the  $K_d\text{Sr}$  values for *C. vulgaris* are similar to those from some skeletal HMC grown in seawater (i.e.  $K_d\text{Sr} = 0.326$  for red algae) or they fall within the range 0.26–0.43 for HMC from diverse invertebrates [37].

No significant changes in  $K_d\text{Sr}$  for abiotic calcites have been calculated for the temperature range 10–40°C [30]. Nevertheless, temperature seems to influence the Sr uptake in biogenic calcites from some ostracod [38] and foraminifera [39] species. In our case, the very good fit of the data in the regression line for *C. vulgaris* may indicate that there are no significant temperature effects on Sr uptake in charophyte calcite for this species at least over the range 18–28°C which is the estimated water temperature range for the calcification period of the diverse aquatic environments listed in Table 1.

## 5. Conclusions

Intra-specific and species-to-species mineralogical variations of the gyrogonites and stem encrustations are present within the genus *Chara*. Moreover, polymineral calcification is present within single oogonial cells. The data indicate strong specific differences in the biological mechanisms of mineralization within this group of plants, and



the need for further research on the formation and ultrastructural features of charophyte calcifications.

There is an overall relationship between the mineralogy of the charophyte carbonates and the Mg/Ca ratio of the water in which they formed. Nevertheless, for various species of the genus *Chara* studied, no correlation exists between the charophyte carbonate mineralogy and the salinity of water where they thrived. The Sr/Ca in the charophyte carbonates studied seems to reflect directly the Sr/Ca of the water where they formed in the range 18–28°C, whereas Mg/Ca in these carbonates depends on the Mg/Ca<sub>w</sub> and other environmental parameters, such as temperature. Moreover, we report partitioning coefficients of Sr and Mg for charophyte calcite for individual species.

This study illustrates the importance of determining the mineralogy of charophyte carbonates to be used for paleoenvironmental studies, especially in δ<sup>18</sup>O investigations of continental climate, and documents the potential application of the Sr and Mg contents in charophyte Ca–Mg carbonates for reconstructing the Sr/Ca and Mg/Ca of the water in which they formed. These results provide new insights and promising perspectives in the use of charophyte carbonates as paleoenvironmental proxies for Pliocene and Quaternary lake records.

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