



Invited Review Article

The many types of carbonic anhydrases in photosynthetic organisms

Robert J. DiMario^a, Marylou C. Machingura^b, Grover L. Waldrop^b, James V. Moroney^{b,*}^a School of Biological Sciences, Molecular Plant Sciences, Washington State University, Pullman, WA 99164, United States^b Department of Biological Sciences, Louisiana State University, Baton Rouge, LA 70803, United States

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ABSTRACT

Carbonic anhydrases (CAs) are enzymes that catalyze the interconversion of CO₂ and HCO₃⁻. In nature, there are multiple families of CA, designated with the Greek letters α through θ . CAs are ubiquitous in plants, algae and photosynthetic bacteria, often playing essential roles in the CO₂ concentrating mechanisms (CCMs) which enhance the delivery of CO₂ to Rubisco. As algal CCMs become better characterized, it is clear that different types of CAs are playing the same role in different algae. For example, an α -CA catalyzes the conversion of accumulated HCO₃⁻ to CO₂ in the green alga *Chlamydomonas reinhardtii*, while a θ -CA performs the same function in the diatom *Phaeodactylum tricornutum*. In this review we argue that, in addition to its role of delivering CO₂ for photosynthesis, other metabolic roles of CA have likely changed as the Earth's atmospheric CO₂ level decreased. Since the algal and plant lineages diverged well before the decrease in atmospheric CO₂, it is likely that plant, algae and photosynthetic bacteria all adapted independently to the drop in atmospheric CO₂. In light of this, we will discuss how the roles of CAs may have changed over time, focusing on the role of CA in pH regulation, how CAs affect CO₂ supply for photosynthesis and how CAs may help in the delivery of HCO₃⁻ for other metabolic reactions.

1. Introduction – the CA catalyzed reaction

Carbonic anhydrase (CA) is an enzyme that catalyzes the interconversion between CO₂ and HCO₃⁻ in solution as well as other reactions [1]. While the CO₂ and HCO₃⁻ conversion does take place in the absence of CA, the interconversion is very slow. It is thought that CA is required to ensure a rapid supply of CO₂ and HCO₃⁻ for various metabolic pathways in organisms.

2. There are multiple, apparently unrelated CA families

There are a surprisingly wide variety of CA proteins that fall into a number of protein families. These families are named by Greek letters and roughly follow the order in which they were discovered. The first class, the α -CA, was discovered in the 1930's in vertebrates. Work characterizing plant CAs in the early 1990s recognized this second group as a new type of CA [2,3]. A third group was identified in archaeobacteria in 1994 [4] and for a brief time the three protein families were referred to as the animal, plant and archaea CA forms. However, the discovery of both α - and β -CAs in *Chlamydomonas reinhardtii* and in terrestrial plants quickly showed that better terminology was needed and the Greek letters were quickly adopted [5]. The latest CA families, the η -CAs [6] and the θ -CAs [7,8], were discovered in 2015 and 2016,

respectively. It should be emphasized that each protein family appears to be phylogenetically unrelated to the others unless noted. In other words, when one compares the sequence or structure of the α - and γ -CA classes, there is often little to no sequence similarity or structural similarity [1]. Even the amino acids coordinating the Zn ions in the CA active sites are not conserved. However, in some cases the active site of some CAs are quite similar. For example, ζ and θ -CAs are structurally analogous to β -CAs at the active site while the active site of δ -CAs are similar to α -CAs.

2.1. Alpha CAs

The first CA was isolated from erythrocytes and later became known as a member of the α -CA class [9,10]. The α -CA is found in plants, green algae, diatoms, cyanobacteria and animals and is distinct from all other CA classes in both protein structure and amino acid sequence. The protein structure of α -CAs is dominated by a central β -sheet consisting of ten β -strands surrounded by seven peripheral α -helices [11]. The central β -sheet houses the active site of the α -CA, coordinating the zinc atom with three histidine residues and a water molecule [11]. Historically, the α -CA is regarded as the only CA class to not form multimers, but a few recent studies report the dimerization of α -CA monomers [12–14].

* Corresponding author.

E-mail addresses: robert.dimario@wsu.edu (R.J. DiMario), mmaching@lsu.edu (M.C. Machingura), gwaldro@lsu.edu (G.L. Waldrop), btmoro@lsu.edu (J.V. Moroney).

2.2. Beta and epsilon CAs

The first report speculating the presence of CA in plants emerged in 1936 [15] but CA activity in plants was not observed in plants until 1939 when Arthur Neish successfully measured CA activity in isolated chloroplasts and whole leaf extracts of *Trifolium pretense*, *Arctium minus*, and *Onoclea sensibilis* [16]. The discovery that the prominent chloroplast CA is distinct from the α -class CA occurred much later via protein sequence analysis, and these CAs are now known as β -CAs [2,3,17]. The β -CAs are found in plants, algae, cyanobacteria, and non-photosynthetic bacteria but are excluded from animals. The β -CA monomer is distinct from α -CAs as it is mainly composed of α -helices that surround a central β -sheet comprised of four parallel β -strands [18]. β -CA monomers oligomerize to dimers to form two active sites consisting of a zinc atom coordinated by two cysteine residues, a histidine residue, and a water molecule [18]. These dimers can further interact to form tetramers and octamers [18,19]. ϵ -CAs are found in cyanobacteria and are now recognized as being a highly modified β -CA [20,21]. ϵ -CAs not only have an enzymatic function, they also form a structural part of the carboxysome shell in cyanobacteria [20].

2.3. Gamma CAs

γ -CAs were first discovered in the archaeon *Methanosarcina thermophila* [4]. Plants [22] and photosynthetic bacteria [23,24] also contain γ -CAs, whereas no reports have emerged detailing γ -CAs in animals. The archaeobacterial γ -CA possesses a zinc active site coordinated by three histidine residues and one water molecule [25]. To form the γ -CA active site, one monomer provides two zinc-coordinating histidine residues whereas a second monomer provides the third zinc-coordinating histidine residue [25]. Altogether, three monomers interact to form three active sites per homotrimer, the active γ -CA unit. The cyanobacterial protein CcmM is also a γ -CA, although modified. The N-terminus of CcmM has a γ -CA domain while the C-terminus has three to four RbcS domains allowing the protein to coordinate Rubisco packaging in the carboxysome. Espie and colleagues have shown that some CcmM proteins are enzymatically active CAs while others lack CA activity although they are still important in carboxysome packaging [26]. Those cyanobacteria with inactive CcmM proteins always have a β -CA in the carboxysome to convert HCO_3^- to CO_2 for Rubisco. In terrestrial plants, γ -CAs and γ -like CAs have been shown to be part of complex I of the mitochondria. Disruption of two γ -CA genes leads to loss of complex I. Green algae and diatoms also have γ -CAs localized to the mitochondria. However none of the CAs from eukaryotic algae or plants have been shown to have CA activity at this time.

2.4. Delta and zeta CAs

To date, δ -CAs and ζ -CAs have only been reported in diatoms and coccoliths [27,28]. The δ -CA, TWCA1 was reported in 1997 while the ζ -CA, CDCA1 was reported a few years later [29]. To date these CAs have not been found in other algae, even pennate diatoms. The Zn-binding region of CDCA1 is repeated three times and its structure was reported in 2012 [30]. An unusual aspect of the CDCA1 is its ability to use other metals besides Zn. Activity has been reported for this ζ -CA when binding others metals, most notably Cd. This ability to bind other metals might be an evolutionary adaptation to the low Zn levels often found in oceanic environments.

2.5. Eta CAs

Another new type of CA was reported in 2015. This CA, named an η -CA, was reported in the protozoan *Plasmodium falciparum* [31]. The structure of this η -CA has not been resolved yet, although the Zn coordination pattern is reported to be distantly related to that of α -CAs [32].

2.6. Theta CAs

θ -CAs are the most recent group of CAs reported. The θ class of CA has recently been described in the diatom *Phaeodactylum tricornutum* [7], the chlorophyte, *C. reinhardtii* [8] and the cyanobacterium *Chlorothece* [8]. In the diatom *P. tricornutum*, at least one of the θ -CAs, Pt43233, is localized to the thylakoid lumen [7]. Its function appears to be to catalyze the formation of CO_2 from the HCO_3^- pool in the diatom chloroplast. Since the pH of the thylakoid lumen is below the pKa of the CO_2 to HCO_3^- interconversion, this enzyme would tend to produce CO_2 from any HCO_3^- transported into the thylakoid. The loss of this protein results in a diatom growing slowly on air levels of CO_2 and showing a reduced affinity for inorganic carbon [7]. The other well-studied member of this CA family is the LCIB/LCIC complex of *C. reinhardtii* [8]. The *LCIB* gene (previously referred to as *Pmp*) encodes a θ -CA which is a chloroplast stromal protein surrounding the chloroplast pyrenoid [33]. Loss of *LCIB* results in a *C. reinhardtii* strain with a disabled CCM that requires high CO_2 concentrations for growth and photosynthesis [34]. *LCIB/LCIC* is thought to recapture CO_2 leaking out of the pyrenoid and possibly direct the HCO_3^- formed back into the pyrenoid [35].

3. CAs have a broad distribution in plants and algae

The CA enzyme is ubiquitous in nature although only certain classes of CA may be present in a particular organism. A distribution of the various CA classes is shown in Table 1. The focus of this table is to show whether a CA class is present in a group of plants or algae, but other selected model organisms are also shown for comparison. Since the sampling of many of the algal groups is limited to one or two genomes at this time, the absence of a specific class of CA in a specific lineage may not mean that all algae in that group lack that CA class. The origins of the α -, β - and γ -CA classes are ancient with all three CA types being found in bacteria, plants and many eukaryotic algal lineages. The ϵ -CA,

Table 1

Distribution of CAs in different lineages. One or more protein from each CA group was used to probe the genome sequences of each species using tBLASTn. Each species is only listed as having (+) or not having (–) a gene that encodes a protein related to that CA type. A species that is positive for a CA type may have multiple genes.

Taxa	Species	α CA	β CA	γ CA	δ CA	ζ CA	θ CA
Land plants	<i>Arabidopsis thaliana</i>	+	+	+	–	–	–
	<i>Oryza sativa</i>	+	+	+	–	–	–
Chlorophytes	<i>Chlamydomonas reinhardtii</i>	+	+	+	–	–	+
	<i>Coccomyxa subellipsoidea</i>	+	+	+	–	–	+
Prasinophytes	<i>Ostreococcus lucimarinus</i>	–	+	–	+	–	+
	<i>Micromonas pusilla</i>	–	+	+	–	+	+
Rhodophytes	<i>Chondrus crispus</i>	+	+	+	–	–	–
	<i>Galdieria sulphuraria</i>	+	–	+	–	–	–
Haptophyte	<i>Emiliania huxleyii</i>	+	–	+	+	–	+
Bacillariophytes	<i>Thalassiosira pseudonana</i>	+	–	+	+	+	+
	<i>Phaeodactylum tricornutum</i>	+	+	+	–	–	+
Phaeophyte	<i>Saccharina japonica</i>	+	+	–	–	–	–
Cryptomonad	<i>Guillardia theta</i>	+	+	+	–	–	+
Heterokont	<i>Aureococcus anophagefferens</i>	–	–	+	+	–	–
	<i>Escherichia coli</i>	–	+	+	–	–	–
Vertebrates	<i>Homo sapiens</i>	+	–	–	–	–	–
	<i>Mus musculus</i>	+	–	–	–	–	–
Insect	<i>Drosophila melanogaster</i>	+	–	–	–	–	–
	<i>Dictyostelium discoideum</i>	–	+	+	–	–	–
Fungi	<i>Saccharomyces cerevisiae</i>	–	+	–	–	–	–
	<i>Aphanomyces invadans</i>	+	+	+	–	–	–
Cyanobacteria	<i>Synechocystis</i> sp. PCC 6803	–	+	+	–	–	–
	<i>Cyanothece</i> sp. PCC8801	+	+	+	–	–	+
Archaea	<i>Sulfolobus acidocaldarius</i> DSM 639	–	–	+	–	–	–

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