12.007 Geobiology
Spring 2009

Lecture 13

Chitin ($C_8H_{13}O_5N)_n$ (pronounced /ˈkaɪtən/) is a long-chain polymer of a N-acetylglucosamine, a derivative of glucose, and it is found in many places throughout the natural world. It is the main component of the cell walls of fungi, the exoskeletons of arthropods, such as crustaceans (like the crab, lobster and shrimp) and the insects, including ants, beetles and butterflies, the radula of mollusks and the beaks of the cephalopods, including squid and octopuses. Chitin has also proven useful for several medical and industrial purposes. Chitin is a biological substance which may be compared to the polysaccharide cellulose and to the protein keratin. Although keratin is a protein, and not a carbohydrate, both keratin and chitin have similar structural functions.

Keratin **Keratins** are a family of fibrous structural proteins; tough and insoluble, they form the hard but nonmineralized structures found in reptiles, birds, amphibians and mammals. They are rivaled as biological materials in toughness only by chitin.

There are various types of keratins within a single animal. Keratins are the main constituent of structures that grow from the skin:

- the *α-keratins* in the hair (including wool), horns, nails, claws and hooves of mammals[*verification needed*]
- the harder *β-keratins* in the scales and claws of reptiles, their shells (chelonians, such as tortoise, turtle, terrapin), and in the feathers, beaks, and claws of birds.[*verification needed*] (These keratins are formed primarily in beta sheets. However, beta sheets are also found in α-keratins.)[1]

Arthropods such as crustaceans often have parts of their armor or exoskeleton made of keratin, sometimes in combination with chitin.

The baleen plates of filter-feeding whales are made of keratin.

They can be integrated in the chitinophosphatic material that makes up the shell and setae in many brachiopods.

Keratins are also found in the gastrointestinal tracts of many animals, including roundworms (who also have an outer layer made of keratin).

Although it is now difficult to be certain, the scales, claws, some protective armour and the beaks of dinosaurs would, almost certainly, have been composed of a type of keratin.

In Crossopterygian fish, the outer layer of cosmoid scales was keratin.

Collagen is the main protein of connective tissue in animals and the most abundant protein in mammals,[1] making up about 25% of the whole-body protein content.

Expectations after an extinction: derive from equations

carbonate carbon – not too much variation

Sulfur isotopes are linked to carbon cycle: sketch of the oceans before and after the oxidation

Neoproterozoic – correlations in the C and S cycle

Global correlation of $d^{13}C_{carb}$ (carbonate, see Supplementary Information for carbon and sulphur isotope nomenclature) anomalies provides two age constraints for the Buah Formation (Fig. 1):,550 Myr for the mid-Buah (correlation with Doushantuo Formation, China[7,9]), and ,548 Myr for the upper Buah (correlation with Nama Group, Namibia[7,8]). These correlations are supported by multiple ages[7] spanning 541– 547 Myr ago obtained from the overlying Ara Group.

The Shuram Formation preserves a .15% negative excursion in $d^{13}C_{carb}$, reaching a minimum of about 212%. The excursion spans 500m of stratigraphic section[16] and is the largest known perturbation to the global carbon cycle in Earth history.

The Shuram excursion is fundamentally different from all known $d^{13}C_{carb}$ excursions (for example the Marinoan cap carbonate, the Ediacaran/Cambrian boundary and the Permian/Triassic boundary), in that $d^{13}C_{carb}$ reaches well below the mantle value of about 26%. Because $d^{13}C_{carb}$ values below -6% cannot readily be explained by changes in organic carbon burial or isotope fractionation during carbon fixation[4], the Shuram excursion was initially attributed to diagenetic alteration of the $d^{13}C_{carb}$ signal[16,21]. However, standard methods of assessing diagenesis (see Supplementary Fig. S2a, b, and discussion in Supplementary Information) indicate that these samples retain primary $d^{13}C_{carb}$ values. Furthermore, the Shuram excursion is now documented in more than 30 sections in Oman, covering a region in excess of 10^5 km^2 with little variation in either magnitude or duration[16,21,23].

$Dd^{34}S$, the difference between coeval $d^{34}S_{SO4}$ (carbonate-associated sulphate) and $d^{34}S_{pyr}$ (pyrite)

Examination of the Huqf Supergroup, Sultanate of Oman, reveals a three-stage oxidation of the Ediacaran ocean. The first stage corresponds to an increase in sulphate concentrations (.200 mM) after the Marinoan glaciation, due in part to an increase in atmospheric oxygen.

The second stage consists of the Shuram excursion and the oxidation of a deep-ocean DOC reservoir, probably the last major redox barrier to ocean oxygenation. This stage is coincident with the appearance of complex acanthomorph acritarchs and motile metazoa.

The final stage of Ediacaran oxidation is characterized by strong signals of BSD and covariation in $d^{13}C_{carb}$ and $d^{13}C_{org}$, coincident with an increase in the diversity of acanthomorph acritarchs and the first appearance of the calcifying metazoa Namacalathus and Cloudina. Taken together, these data record the progressive oxygenation of the Ediacaran ocean, stimulating the evolution of both planktic and benthic groups of organisms.

Carbon isotopic and sequence-stratigraphic data imply that the spectacular animal fossils of the Doushantuo Formation are for the most part younger than 580 million years old. The uppermost Doushantuo Formation contains a pronounced negative carbonate carbon isotopic excursion, which we interpret as a global event at circa 551 million years ago.

The **Bilateria** are all animals having a bilateral symmetry, i.e. they have a front and a back end, as well as an upside and downside. Radially symmetrical animals like jellyfish have a topside and downside, but no front and back. The bilateralians are a subregnum (a major group) of animals, including the majority of phyla; the most notable exceptions are the sponges and cnidarians. For the most part, Bilateria have bodies that develop from three different germ layers, called the endoderm, mesoderm, and ectoderm. From this they are called triploblastic. Nearly all are bilaterally symmetrical, or approximately so. The most notable exception is the echinoderms, which are radially symmetrical as adults, but are bilaterally symmetrical as larvae.

Except for a few primitive forms, the Bilateria have complete digestive tracts with separate mouth and anus. Most Bilateria also have a type of internal body cavity, called a coelom. It was previously thought that acoelomates gave rise to the other group, but there is some evidence now that in the main acoelomate phyla (flatworms and gastrotrichs) the absence could be secondary. The indirect evidence for the primitivity of the coelom is that the oldest known bilaterian animal, Vernanimalcula, had a structure that could be interpreted as a body cavity.

The basic body shape of a cnidarian consists of a sac containing a gastrovascular cavity with a single opening that functions as both mouth and anus . It has radial symmetry, meaning that whichever way it is cut along its central axis, the resulting halves would always be mirror images of each other. Their movement is coordinated by a decentralized nerve net and simple receptors. Several free-swimming Cubozoa and Scyphozoa possess rhopalia, complex sensory structures that can include image-forming eyes with lenses and retinas

Ctenophorans are diploblastic (having only two body layers). The body consists of two transparent cell layers, which make up its outer skin (ectoderm) and inner skin (gastroderm). The ectoderm, made up of two cell layers, is mostly covered by a protective layer of slime, excreted by special glands. The gastroderm surrounds a cavity which serves as a stomach and is only accessible by the mouth opening, connected by a long, narrow gullet. Captured quarry is pre-digested in the gullet by strong enzymes and fully decomposed in the stomach. There is no separate exit from the stomach apart from two 'anal pores', which despite their name appear to be only moderately used for excretion, so indigestible waste is principally expelled via the mouth.

Sponges are widely recognised (*e.g*. Nielsen 2001, pp. 30, 506-507) to be the most primitive of living metazoans, occupying a basal position in metazoan phylogeny, as a sister group to all other Metazoa. Thus their first occurrence in the fossil record is a metric of particular interest. However, only rare occurrences of Precambrian sponges have been reported. The earliest record is of presumed sponge remains from the Doushantuo phosphates, dated around 570 Ma (Li *et al*. 1998), and the earliest described species is Paleophragmodictya reticulata from the ?555 Ma Ediacara locality. However, sponges could have occurred earlier and not been recognised; spicules are not necessarily diagnostic, even in living sponges (Dr. Allen Collins, *pers. comm*.

Li *et al.* 1998 proposes that the Doushantuo sponges are monaxonid Demospongiae because their skeleton consists exclusively of siliceous and monaxonal spicules. However, it is generally interpreted that Hexactinellida evolved before both Calcarea and Demospongiae, and the recently discovered Ediacarian sponges from Mongolia (Brasier et al. 1997) are also referred to Hexactinellida.

The Weng'an sponge remains of Doushantuo age (Early Vendian), therefore may require revision of phylogenetic relations among the four major classes of phylum Porifera. Sponges are a monophyletic metazoan group and comprise the sister groups demosponges, hexactinellids, archaeocyaths, and calcareous sponges. Our data imply that the ancestral form in sponges lies among the demosponges.

Sponges are a major component in Lower Cambrian Chengjiang fauna. There, the skeletons in most species are represented exclusively by diactins, which form a regular, reticulate skeletal framework, and these fossils are classified as demosponges. The data from Chengjiang fauna demonstrate that main clade of early sponges, the monaxonid Demospongiae was diverse in the Lower Cambrian. Li et al. 1998 conclude that diactins evolved before other types of spicules.

Analysis of the associated rocks suggests that in the Late Proterozoic, silica biomineralization in the sponges happened in an eutrophic environment. Calcareous biomineralization in sponges (for example, archaeocyathids) is first seen in the Tommotian (~530 Ma), postdating the silica biomineralization by more then 50 million years. Calcareous biomineralization is mainly seen in oligotrophic settings. Archaeocyathids, which are possible representatives of coralline sponges, have a secondary calcareous skeleton of high Mg-calcite and are possibly derived from demosponges.

Reproduction of fig. 1A from Li *et al*. 1998; a possible longitudinal section of a tubular phosphatized sponge, showing the randomly dispersed monaxonal spicules (s) in the mesohyl (m). Two spicules firmly associated with spicule-producing cells, the scleocytes, are encircled. Scale bar is 100 µm.

(B) Reproduction of fig. 1F from Li *et al*. 1998; two sclerocytes (sc) with their developing spicules (s) and plasma membrane (pm). Scale bar is 10 µm.

(C) Reproduction of fig. 2D from Li *et al*. 1998; a proposed embryo at the blastula stage. Scale bar is 50 µm.

The *Vernanimalcula* fossils were discovered in the Doushantuo Formation in China. This formation is a *Lagerstätte*, one of the rare places where soft body parts and very fine details are preserved in the fossil record. The *Vernanimalcula* fossils show triploblastic structure, a coelom, a differentiated gut, a mouth, an anus, and paired external pits that could be sense organs.

calcified organisms – ecological diversification – live close to microbial mats but not binding the sediment – different mode of living

Some, such as the German paleontologist Adolph (Dolf) Seilacher, have expressed doubts that the 'quilted' Ediacarans were animals at all; suggesting instead that they represent a quite separate evolutionary lineage. In spite of their apparent diversity, nearly all of the genera share a striking basic uniformity: they are thin and flattened, round or leaf-like, possess a ridged or 'quilted' upper surface, and lack clear indications of a mouth or gut. Seilacher believes that the Ediacaran body plan comprises tough organic walls surrounding fluid-filled internal cavities.

However, most workers reject this idea. "It's clearly not true for, say, the Burgess Shale. Why should it apply to the Ediacarans?" (Waggoner 1999).

In view of the fauna's supposed primitive metazoan affinities, the virtual absence of sponges (phylum Porifera) is intriguing. However, rare occurences of sponges *have* been reported: Gehling & Rigby 1996 describes a probable sponge, *Paleophragmodictya* from the Ediacaran of South Australia (read more)

and Li et al. 1998 reports sponge remains from the extremely ancient Doushantuo phosphate deposit in China, which predates any known Ediacaran assemblage (read more).

- **Domichnia** are dwelling structures that reflect the life position of the organism that created it. Examples of Domichnia are *Arenicolithes* and *Skolithos*.
- **Fodinichnia** are three-dimensional structures left by animals which eat their way through sediment, such as deposit feeders;
- **Pascichnia** are another type of feeding trace, left by grazers on the surface of a soft sediment or a mineral substrate;
- **Cubichnia** are resting traces, in the form of an impression left by an organism on a soft sediment;
- **Repichnia** are surface traces of creeping and crawling, as an organism moved from one station to another.

the absence of tracks or trails of larger arthropods, or of sinusoidal nematode trails, which could well be preserved and easily recognized. Even small benthic arthropods appear to have been absent, because they would likely have destroyed the biomats and produced a flocculent surface layer

why do things create traces?