Journal of Water Resources and Ocean Science
2019; 8(6): 86-93
http://www.sciencepublishinggroup.com/j/wros
doi: 10.11648/j.wros.20190806.11
ISSN: 2328-7969 (Print); ISSN: 2328-7993 (Online)

The Ancient Shells Were Studied by X-ray Diffraction and Electron Probe

Chen Junhao, Chen Guiqing

Institute of Technology, Jinan University, Guangzhou, China

Email address:
c2816@126.com (Chen Junhao), 814713052@qq.com (Chen Guiqing)

To cite this article:
Chen Junhao, Chen Guiqing. The Ancient Shells Were Studied by X-ray Diffraction and Electron Probe. *Journal of Water Resources and Ocean Science*. Vol. 8, No. 6, 2019, pp. 86-93. doi: 10.11648/j.wros.20190806.11

Received: September 27, 2019; **Accepted**: October 17, 2019; **Published**: November 5, 2019

Abstract: What changes have they made since the shells were buried in the ground for thousands of years? The geological crystallography book records that the physical properties of the aragonite structure are unstable and will eventually be converted into calcite. This is probably also a theory copied from abroad, and no one in the country has ever studied it. The crystal structure of the test substance can only be measured by an X-ray diffractometer, and geologists seem to not be familiar with crystallography. Now I plan to use X-ray diffraction to verify the correctness of this theory? It turns out that after a long geological time, not only did the aragonite not become calcite, but the grain grew up again - "single crystal" and even calcite decreased, proving that this theory is wrong. Carbon 14 (C^{14}) is used to determine the geological age of some artifacts. Now using the electronic probe to detect the "double Chen weathering hole CC" of the ancient shell, it may be used as another method to determine the geological time.

Keywords: Marine Biology, X-ray Diffraction, Aragonite Structure, Calcite Structure, WDX-Electron Probe, CC-double Chen, Weathered Hole

1. Foreword

What changes will happen to shells after they have been buried in the ground for thousands of years? The geological crystallography textbook [4, 5] records that the physical properties of the meteorite structure are unstable and will eventually turn into calcite. This has become a common sense and can be found on any Internet. If the crystal structure really changes, it will be a long process, the vergeite lattice constant will gradually become distorted, and finally become the calcite structure!

Aragonite gemstones are composed of aragonite (also known as aragonite in crystallography), calcite, iron oxide, and opal. They are secondary minerals and aragonite is one of the main components. In the world, only China's Tibet, Taiwan's Penghu Islands and Italy's Sicily produce aragonite gemstones. According to the above theory, aragonite does not seem to exist in the world, because the aragonite structure contained in these minerals has been transformed into calcite structure after hundreds of millions of years, but in fact they still exist! We have detected that the lattice constant of the aragonite structure gradually transforms into the deformed lattice of the calcite structure at high temperature, but under deep sea high pressure, the *Abra profundorum* shell and the *nautilus pampilium* L shell are still aragonite crystals. The aragonite structure is stable under high pressure, which also questions the correctness of this theory. We now use x-ray diffraction to detect the crystal structure of ancient shells, to see if the aragonite or calcite distortion lattice constant can be detected? In order to verify the correctness of the above theory!

The use of electronic probes to detect ancient shells has revealed many weathering holes that vary with the geological age. We call it the “double Chen weathering hole CC”, which may be used as another method to determine the geological time.

2. Materials and Methods

2.1. X-ray Diffraction

In the 1980s, researchers from nanjing institute of paleontology, huang baoyu, provided four kinds of ancient shells: clams with split teeth, clams with split riblets, mussels with domed shells and mussels with beautiful shells. In 2016, tan yehui, a researcher at the south China sea institute of oceanology, Chinese Academy of Sciences, provided four kinds of ancient shells, including tridacna, tridacna, pipi and clams. The crystal structure was determined by X - ray diffractometer. Aragonite structure conforms to 04-1475 [6]; Calcite structure is consistent with 24-27 [6].

2.2. Electron Microprobe Discuss

Materials as before; The electron probe method was used in the study by south China sea institute of oceanology, Chinese Academy of Sciences.

3. Results and Discussion

3.1. Experimental Results of X-ray Diffraction

In Table 1, the lower bar line such as 0.3400 corresponds to the card 041-1475 [6], which is the aragonite line; the lower dotted line such as 0.3038 corresponds to the card 24-27 [6], which is the calcite line; the lower point, the bar, the point line line 0.3336 is the silica line. The line will drift somewhat due to detection conditions, zero calibration, etc. The same is true of the following.

3.1.1. Schistodesmus sp. Prismatic Layer

102 West Point Village, field number ADY201, 1983/9/9. Age: hundreds of years to thousands of years.

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

3.1.2. Schistodesmus Lampreyanus (Baird & Adams) Prismatic Layer

102, Kenting Village, Shanxi, 1986/12/16. Age: hundreds of years to thousands of years.

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

3.1.3. Unio Douglasiae (Gray)

Field number ADY201, 12/16, 1986/12/16. Years: hundreds to thousands of years.

(i). Unio Douglasiae (Gray) Pearl Layer

Most of the spectral lines conform to the card 041-1475, It's almost all aragonite structure

The only occurrence of calcite weak line d_{104}=0.3038nm, I/I_0=1.64%, containing calcite 0.15% [12]. It's too weak, it's probably stuck, because the stratum corneum does not have it.

(ii). Unio Douglasiae (Gray) Periostracum

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

3.1.4. Lamprotula sp.

Field number ADY193, 1986/12/16. Age: hundreds of years to thousands of years.

(i). Lamprotula sp. Pearl Layer

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

(ii). Lamprotula sp. Prismatic Layer

Most of the spectral lines conform to the card 041-1475, it's almost all aragonite structure.

The only occurrence of calcite weak line d_{104}=0.3034nm, I/I_0=2.6%, containing calcite 0.23%. It's too weak, it's probably stuck.

(iii). Lamprotula sp. Periostracum

Most of the spectral lines conform to the card 041-1475, it's almost all aragonite structure.

The only occurrence of calcite weak line d_{104}=0.3024nm, I/I_0=1.7%, containing calcite 0.17%. It's too weak, it's probably stuck,

(iv). Modern Lamprotula sp. Pearl Nuclei

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

There is no difference in spectroscopy between modern shells and ancient shells

3.1.5. Trapezium Liratum (Reeve) Periostracum

Guangdong Shunde Longbei Lunjiao Brigade Yuan Zhou production team 1 well Quaternary loose sedimentary rock center. Collectors: Wu Wenzhong, Zhao Huan Ting. Acquisition time: early 1970s. Year: 500-1000 years ago. Measurement date / time 2015-11-27 8:48:35.

Most of the spectral lines conform to the card 041-1475, it's almost all aragonite structure.

There are two strong silica lines d=0.3370nm, I/I_0=70.2%; d=0.1824nm, I/I_0=55.96%, which is the silica that the ancient shells have adhered to in the soil for many years. Because modern shells never see these lines.

3.1.6. Potamacorbula Laevis (Hinas) Periostracum

Guangdong Shunde Longbei Lunjiao Brigade Yuan Zhou production team 1 well Quaternary loose sedimentary rock center. Collectors: Wu Wenzhong, Zhao Huan Ting. Acquisition time: early 1970s. Year: 500-1000 years ago. Measurement date/time: 2015-11-27/9:01:27.

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

3.1.7. Corbicula Fluminea (Müller)

Guangdong Shunde Longbei Lunjiao Brigade Yuan Zhou production team 1 well Quaternary loose sedimentary rock center. Collectors: Wu Wenzhong, Zhao Huan Ting. Acquisition time: early 1970s. Year: 500-1000 years ago. Measurement date / time 2015-11-27 9:14:37

(i). Corbicula Fluminea (Müller) Prismatic Layer

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

(ii). Corbicula Fluminea (Müller) Periostracum

Most of the spectral lines conform to the card 041-1475, it's almost all aragonite structure.

The strongest spectral line d=0.3336nm is the strongest line of silica SiO_2 d_{101}=0.33435 nm, and the spectral line d=0.4249 nm is the second strongest spectral line of silica SiO_2 d_{100}=0.4255 nm. This is the silica that the ancient shells were buried in the soil for many years and therefore adhered. Modern shells have never seen these spectral lines.

Two weak calcite spectral lines appeared: d_{104}=0.3033 nm, I/I_0=8.71% and d_{113}=0.2282 nm, I/I_0=7.26%, containing calcite 0.77%. It's too weak, Two weak calcite spectral lines appeared: d104=0.3033 nm, I/I_0=8.71% and d_{113}=0.2282 nm, I/I_0=7.26%, containing calcite 0.77%. It's too weak, and may be adhered to.

There is also an impurity spectral line d = 0.3205 nm, I / I_0 = 18.38%, I don't know what the substance is, Is also adhesive impurity.

The ancient *Corbicula fluminea* shell is the same as the modern *Corbicula fluminea* shell spectral line.

(iii). Modern Corbicula Fluminea (Müller) Prismatic Layer

Most of the spectral lines conform to the card 041-1475, it's almost all aragonite structure.

The only one weak impurity line d = 0.3632 nm, I / I_0 = 3.21%.

3.1.8. Corbicula Maxima Prime

Unearthed from the water project of Longyan Village, Shunde, Guangdong. Collector: Zhao Huan Ting and so on. Collection time: February 1961. Year: 500-1000 years ago. Measurement date / time 2015-11-27 9:48:41

(i). Corbicula Maxima Prime Pearl Layer

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

From the left side of Figure 1, The strongest spectral line d= 0.2875nm absolute strength is equal to I = 4290.7 (this is the diffraction result of the instrument, omitted in the table. Generally, the strongest intensity of the spectral line of the shell is about 700), It is very strong, very narrow, and has less spectral lines. The conclusion of geological crystallography: the crystal structure of aragonite is unstable, and it will eventually become calcite. Now, on the contrary, it will develop to a higher "aragonite single crystal", indicating the structure of aragonite, it is stable.

From the X-ray diffraction theory of the crystal Scherrer's formula [7]: the spectra line becomes stronger, narrower and has few spectral lines. is due the growth and thickening of the grains in the diffraction direction (preferred orientation growth), we call it "Single crystalization trend".

The growth process of shell pearl layer is the growth process of aragonite crystal. Due to the lattice distortion caused by the vacancy or impurity filling into the crystal lattice, the crystal face family spacing d changes and the spectral line becomes wider. New internal stress is always generated, and the stress is constantly released under the action of stress. When the shellfish die, the crystal stops growing and no new internal stress is created. The internal stress in the shell is gradually released, the vacancy is gradually filled or the impurities are gradually removed to the grain boundary to eliminate the internal stress. At this time, the internal stress is also concentrated on the grain boundary, so it is easy to be weathered away. Aragonite grain grows continuously, so; Make spectral lines stronger, narrower and less!

Because the *Corbicula maxima* shell is larger, it is less affected by the surrounding soil,, more can reflect the growth process.

(ii). Corbicula Maxima Prime Prismatic Layer

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

The strongest line d =0.2709nm absolute strength is equal to I = 3406.3, It is very strong, very narrow, and has less spectral lines. However, because the prismatic layer is between the pearl layer and the periostracum, the internal stress is released slowly, so the spectral line is slightly more, but from its X-ray diffraction pattern, many weak lines have become almost flattening, the development is similar to the pearl layer spectra line.

(iii). Corbicula Maxima Prime Periostracum

All spectral lines conform to card 041-1475, all are aragonite structures and there are no impurities.

From the right side of Figure 1, the absolute intensity of the strongest line d=0.1980nm is the I=481.16, due to the large organic matter in the stratum corneum, affecting the single crysta processl, making absolute The intensity is greatly reduced and the spectral lines are slightly more

The characteristics of the amorphous diffraction pattern are as shown in the figure, and the entire scanning angle range (2θ from 1° -- 2° starts to the several tens of degrees) because the intensity of the near direct beam is large. And the intensity rapidly with the increase of the angle to decrease, to a high angle intensity towards the instrument's background value, there may be one to several peak values. From the point of view of Scherrer's formula [7], this phenomenon can be considered as the grain size is extremely small, and these crystallites are too small to be affected by external forces, and the crystal lattice is differently distorted, resulting in the diffraction peak of the crystal being greatly widened. The result of overlapping and obscuring.

Incoherent scatter occurs when X-rays are incident on the sample, and their intensities are also mainly concentrated in the low angle range, with the result that the background intensity is increased. There is also background scattering from the air.

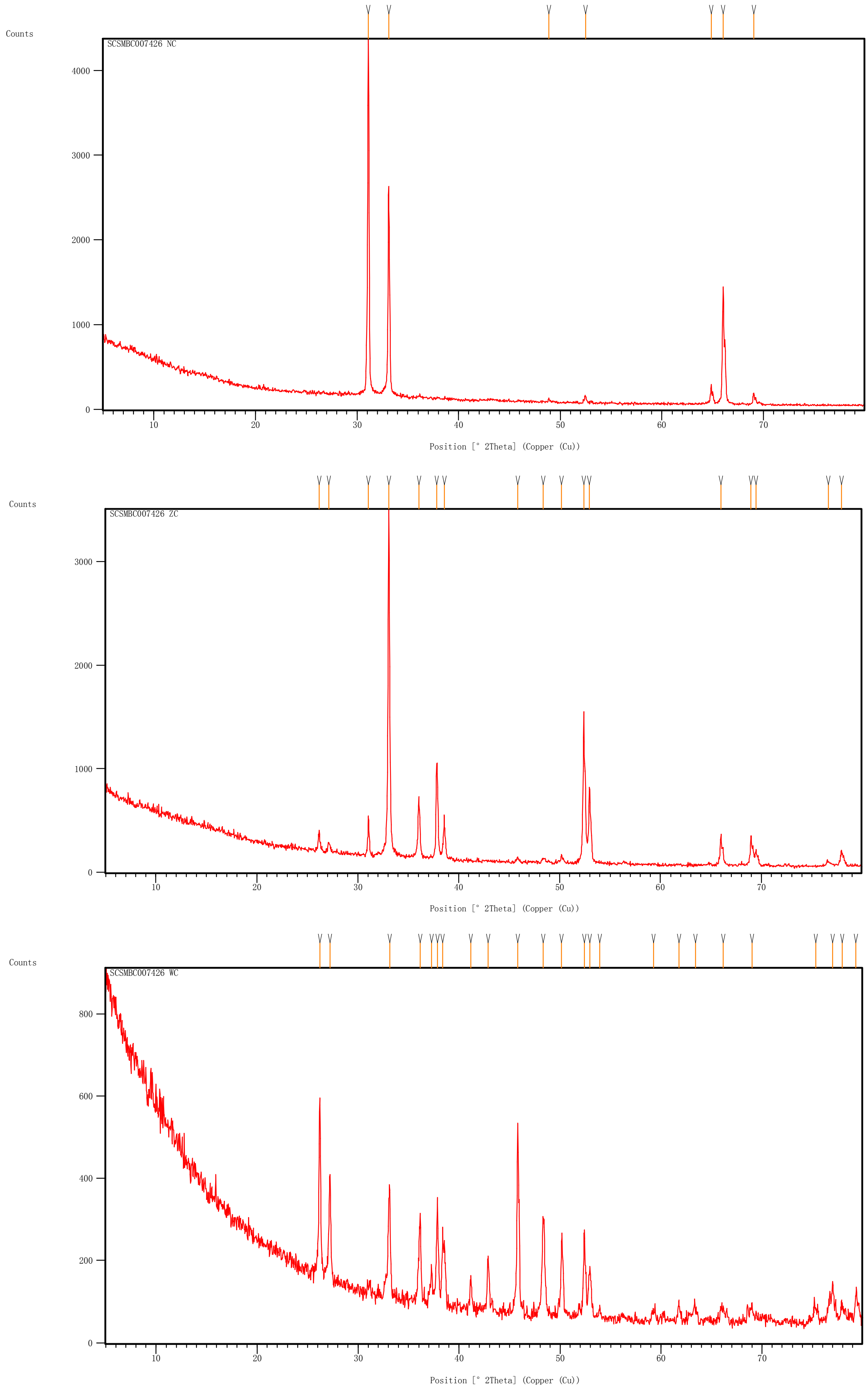

Figure 1. *X-ray diffraction pattern of Corbicula maxima: Left picture pearl layer, Middle picture prismatic layer, Right picture periostracum.*

Table 1. *Shell X-ray diffraction data.*

***Schistodesmus sp.* prismatic layer**		***Schistodesmus lampreyanus* prismatic layer**		***Unio douglasiae* pearl layer**		***Unio douglasiae* periostracum**	
d (nm)	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**
0.3980	2.32	0.3398	73.2	0.3399	66.6	0.3397	100
0.3400	91.4	0.3274	43.6	0.3275	35	0.3274	51.6
0.3275	48.4	0.2702	100	0.3038	1.64	0.2700	63.2
0.2702	100	0.2484	42.9	0.2873	23.5	0.2483	38.3
0.2484	52.9	0.2373	46.9	0.2702	100	0.2371	37.6
0.2373	55.4	0.2332	27.9	0.2484	40.4	0.2335	27.2
0.2335	28.5	0.2105	13.3	0.2373	41.2	0.2105	20.5
0.2105	22.2	0.1976	39.5	0.2332	19.6	0.1976	61
0.1977	52.9	0.1879	22.6	0.1976	34.7	0.1879	34
0.1879	31.1	0.1814	19.5	0.1879	21.8	0.1813	20.6

Lamprotula sp. pearl layer		**Lamprotula sp. prismatic layer**		**Lamprotula sp. periostracum**		**Modern Lamprotula sp. Pearl nuclei**	
d (nm)	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**
0.3993	1.39	0.3401	100	0.4218	19	0.3395	53.9
0.3399	58.9	0.3277	51	0.3397	100	0.3273	31.9
0.3274	31.3	0.3034	2.6	0.3274	51	0.2872	16.8
0.2873	12.9	0.2703	61	0.3024	1.9	0.2700	100
0.2702	100	0.2484	38.3	0.2700	26	0.2483	32.9
0.2484	37.3	0.2373	39.8	0.2482	31.4	0.2371	31.6
0.2373	40.3	0.2387	31.8	0.2372	23	0.2329	18
0.2332	21.7	0.2106	22.3	0.2338	35	0.1976	31.9
0.1976	29.4	0.1977	64.8	0.2104	29.1	0.1878	20.6
0.1879	17.2	0.1880	34.4	0.1976	76.3	0.1813	14.1

Trapezium liratum periostracum		**Potamacorbula laevis periostracum**		**Corbicula fluminea prismatic layer**		**Corbicula fluminea periostracum**	
d (nm)	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**
0.3418	100.00	0.3411	22.68	0.3404	31.86	0.4249	17.42
0.3370	70.20	0.3282	15.70	0.3282	15.23	0.3388	32.23
0.3299	38.08	0.2885	23.50	0.2876	11.04	0.3336	100.0
0.2711	45.46	0.2725	76.00	0.2706	100.0	0.3268	18.22
0.2497	42.98	0.2705	100.00	0.2491	31.42	0.3205	13.38
0.2389	52.35	0.2488	49.58	0.2377	51.42	0.3033	8.71
0.2344	25.26	0.2375	54.28	0.2332	22.73	0.2697	67.10
0.2121	13.89	0.2332	25.17	0.1998	11.92	0.2485	30.65
0.1989	78.70	0.1989	4.15	0.1882	11.69	0.2372	39.83
0.1890	59.93	0.1882	14.25	0.1820	13.38	0.2282	7.26
0.1824	56.00	0.1819	12.82	0.1761	14.13	0.1979	18.54

Modern *Corbicula fluminea* prismatic layer		***Corbicula maxima* Pearl layer**		***Corbicula maxima* prismatic layer**		***Corbicula maxima* periostracum**	
d (nm)	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**	**d (nm)**	**I/I_0 (%)**
0.3632	3.21	0.2875	100.0	0.3407	5.31	0.3399	90.81
0.3409	100.0	0.2706	58.06	0.3287	2.61	0.3279	54.75
0.3285	50.6	0.1862	1.48	0.2879	10.97	0.2703	54.46
0.2709	94	0.1744	2.09	0.2709	100.00	0.2484	46.31
0.2490	42.4	0.1438	5.77	0.2492	16.96	0.2413	20.54
0.2415	13.8	0.1415	32.81	0.2378	27.43	0.2377	56.42
0.2377	53.6	0.1361	3.21	0.2334	13.13	0.2345	36.76
0.2338	28.1			0.1979	1.33	0.2193	16.07
0.2109	18.2			0.1881	1.45	0.2110	28.15
0.1980	52.4			0.1817	2.48	0.1980	100.0
0.1882	30.6			0.1747	42.95	0.1883	50.92

Table 2. *Lattice constant of shell aragonite structure [8-13].*

Lattice constant of ancient shell aragonite structure (nm, nm3)			
Schistodesmus sp. shell prismatic layer	a=0.497, b=0.797, c=0.574, v=0.227	*Trapezium liratum* shell periostracum	a=0.500, b=0.805, c=0.576, v=0.232
Schistodesmus lampreyanus shell prismatic layer	a=0.497, b=0.797, c=0.574, v=0.227	*Potamacorbula laevis* shell periostracum	a=0.500, b=0.799, c=0.575, v=0.230
Unio douglasiae shell pearl layer	a=0.497, b=0.797, c=0.574, v=0.227	*Corbicula fluminea* shell prismatic layer	a=0.497, b=0.799, c=0.575, v=0.228
Unio douglasiae shell	a=0.497, b=0.797, c=0.574, v=0.227	*Corbicula fluminea* shell	a=0.494, b=0.795, c=0.573, v=0.225

periostracum		periostracum	
Lamprotula sp. shell pearl layer	a=0.497, b=0.797, c=0.574, v=0.227	*Corbicula maxima* shell pearl layer	a=0.498, b=0.801, c=0.575, v=0.229
Lamprotula sp. shell prismatic layer	a=0.497, b=0.798, c=0.575, v=0.228	*Corbicula maxima* shell prismatic layer	a=0.498, b=0.801, c=0.576, v=0.230
Lamprotula sp. shell periostracum	a=0.497, b=0.797, c=0.574, v=0.227	*Corbicula maxima* shell periostracum	a=0.496, b=0.799, c=0.575, v=0.228
Lattice constant of modern shell aragonite structure (nm, nm3)			
Pinctada martensi pearl	a=0.496, b=0.796, c=0.574, v=0.227	*Pinctada margaritifera* Shelll pearl layer	a=0.497, b=0.797, c=0.574, v=0.228
Pinctada martensi shell pearl layer	a=0.495, b=0.794, c=0.573, v=0.225	*Pinctada margaritifera* shell prismatic layer	a=0.496, b=0.795, c=0.574, v=0.226
Pinctada martensi shell prismatic layer	a=0.496, b=0.796, c=0.574, v=0.227	*Pinctada chemnitzi* shell pearl layer	a=0.496, b=0.796, c=0.574, v=0.227
Pinctada maximax shell pearl layer	a=0.496, b=0.796, c=0.574, v=0.227	*Pinctada chemnitzi* shell prismatic layer	a=0.495, b=0.794, c=0.573, v=0.226
Pinctada maximax shell prismatic layer	a=0.496, b=0.795, c=0.573, v=0.226	*Haliotis diversicolor* shell	a=0.496, b=0.796, c=0.574, v=0.227
Pteria (Magnavicula) *Penguin* shell pearl layer	a=0.495, b=0.795, c=0.574, v=0.226	*Mytilus edulis* shell	a=0.499, b=0.801, c=0.577, v=0.231
Pteria (Magnavicula) *penguin*shell prismatic layer	a=0.495, b=0.794, c=0.573, v=0.225	*Corbicula fluminca* shell	a=0.498, b=0.800, c=0.576, v=0.230

Table 3. *Calcite content of ancient and modern shells [8-13].*

Calcite content of ancient shells: Well below 1%, it's almost nonexistent					
Schistodesmus sp. Shell prismatic layer	0%	*Lamprotula* sp. Shell prismatic layer	0.23%	*Corbicula fluminea* shell periostracum	0.77%
Schistodesmus lampreyanus shell prismatic layer	0%	*Lamprotula* sp. Shell periostracum	0.17%	*Corbicula maxima* shell pearl layer	0%
Unio douglasiae shell pearl layer	0.15%	*Trapezium liratum* shell periostracum	0%	*Corbicula maxima* shell mprismatic layer	0%
Unio douglasiae shell periostracum	0%	*Potamacor bula laevis* shell periostracum	0%	*Corbicula maxima* shell periostracum	0%
Lamprotula sp. shell pearl layer	0%	*Corbicula fluminea* shell prismatic layer	0%		
Calcite content of modern shells					
Pinctada martensi shell periostracum	100%	*Pinctada chemnitzi* shelll periostracum	100%	*Nerita albicilla* shell	8.52%
Pinctada maxima shell periostracum	100%	*Ostrea rivularis s*hell Most of the majority	100%	*Mytilus edulis* shell	15.19%
Pteria (Magnavicula) Penguin shell periostracum	100%	*Haliotis diversicolor* Shell prismatic laye	8.31%	*Chama dunker* shell	20.03%
Pinctada margaritifera shell periostracum	100%	*Pinna atropurpurea* shell periostracum	14%	*Abra profundorum* shell	14%
Pinctada nigra Shell periostracum	100%	*Haliotis diversicolor* shell	29.92%	Modern *Corbicula fluminca* shell prismatic laye	0
All prismatic layers of pearl shells contain less than 1% of calcite spectral lines.					

3.2. Electron Microprobe Results

Elements with atomic Numbers below 11 (Na) cannot be measured, so; $CaCO_3$ can only be calculated from CaO molecular formula.

$$CaO + CO_2 \rightarrow CaCO_3$$

$$56.0794 \qquad 100.0892$$

$$M_{CaCO_3} = (100.089 \div 56.0794) \times M_{CaO} = 1.78478 \times M_{CaO}$$

For ancient *Schistodesmus* sp. Shell:
Inner layer: M_{CaCO_3} =1.78478×48.165=85.9639;

Surface layer: M_{CaCO_3} =1.78478×45.125=80.5377.

The sam e is true of the following.
In the table summation Σ is equal to the summation calcium carbonate and the rest of the oxide. Modern shells of summation measurement results of electron probe Σ equal to about 100%, not necessarily is 100, this is due to the error due to certain factors, normalized to 100%, but the ancient sea shells Σ and 100% have a certain gap, this is the result of ancient shell one thousand weathering, we define: CC = 100 - Σ for "double chen weathering hole", all the parts of the CC in the shell is not the same, expressed by average. According to our test scores of modern shells, general results: Σ = 98.5, so imagine CC value within 5 negligible, as 0, namely "Double Chen weathering hole" is 0. Because the scope of the electron probe test is very small, the important data need to be measured and averaged.

Will ancient *Schistodesmus sp.* Shell; Ancient *Schistodesmus lampreyanus* shell; Ancient *Unio douglasiae* shell; Ancient *Lamprotula sp.* Shell; Modern *Pinctada fucata* *martensi* shell; Modern *Lamprotula mansuyi* shell; Modern *Coelomactra antiquate* shell; Modern *Tegillarca granosa* shell; Electron Microprobe, results as follows:

Table 4. *Oxide of shell.*

Oxide	Na_2O	K_2O	Fe_2O_3	MnO	SiO_2	MgO	TiO_2	Al_2O_3	CaO	$CaCO_3$	SumΣ	CC	CC
Ancient Schistodesmus sp.													
Inner layer	0.254	0.000	0.000	0.028	0.058	0.040	0.045	0.066	48.165	85.964	86.455	13.54	15.9
Surface layer	0.188	0.024	0.092	0.000	0.571	0.146	0.022	0.142	45.125	80.538	81.723	18.28	
Ancient Schistodesmus lampreyanus													
Inner layer	0.151	0.005	0.000	0.000	0.044	0.034	0.000	0.040	43.156	77.024	77.298	22.70	19.9
Surface layer	0.168	0.008	0.046	0.028	0.103	1.227	0.000	0.046	45.512	81.229	82.855	17.14	
Ancient Unio douglasiae													
Inner layer	0.113	0.026	0.031	0.042	0.029	0.046	0.000	0.061	45.758	81.668	82.016	17.98	19.3
Surface layer	0.104	0.000	0.015	0.028	0.073	0.012	0.000	0.030	44.361	79.175	79.437	20.56	
Ancient Lamprotula sp.													
Inner layer	0.254	0.000	0.092	0.042	0.029	0.000	0.046	46.730	83.403	83.901	83.901	16.10	12.8
Surface layer	0.217	0.005	0.230	0.000	0.059	0.000	0.086	50.298	89.771	90.415	90.415	9.58	
Modern Pinctada fucata martensi													
Pearl layer	0.516	0.007	0.020	0.018	0.038	0.058	0	0.030	55.644	99.313	100.000	0	0
Prismatic layer	0.429	0.023	0.039	0.000	0.000	0.085	0	0.065	55.670	99.360	100.000	0	
Periostracum	0.282	0.039	0.000	0.000	0.019	1.205	0	0.048	55.137	98.409	100.000	0	
Modern Lamprotula mansuyi													
Pearl layer	0.38	0.03	0.08	0.07	0.37	0.06	0	0.11	55.65	99.323	100.423	0	0
Prismatic layer	0.59	0.09	0.06	0.11	0.43	0.05	0	0.12	55.67	99.359	100.809	0	
Periostracum	0.25	0.00	0.00	0.04	0.42	0.03	0	0.08	55.38	98.841	99.661	0	
Modern Coelomactra antiquate													
A region	0.62	0.02	0.03	0.00	0.02	0.04	0	0.05	55.59	99.216	99.996	0	0
B region	0.60	0.03	0.00	0.02	0.03	0.00	0	0.00	55.65	99.323	100.003	0	
Modern Tegillarca granosa													
A region	0.56	0.01	0.00	0.04	0.03	0.07	0	0.03	55.61	99.252	99.992	0	0
B region	0.53	0.01	0.00	0.00	0.00	0.07	0	0.03	55.67	99.360	100.000	0	

Table 5. *Comparison of the "double Chen weathered hole CC" result between Ancient and modern shells.*

Ancient shell species	Oxide summation $\bar{\Sigma}$	Double Chen weathered hole $\overline{CC}$	Moder shell species	Oxide summation $\bar{\Sigma}$	Double Chen weathered hole $\overline{CC}$
Schistodesmus sp.	84.09	15.9	*Pinctada martensi* shell	100.00	0
Schistodesmus lampreyanus	80.08	19.9	*Lamprotula mansuy* shell	100.30	0
Unio douglasiae	80.73	19.3	*Mactra* antiquate shell	100.00	0
Lamprotula sp.	87.16	12.8	*Arca* (Anadara) *granosa* shell	100.00	0

4. Conclusions

1. We studied the X-ray diffraction results of 16 samples of 8 ancient shells and modern shells as shown in Table 1. Most of them are aragonite structures of calcium carbonate, and the crystal grains are relatively large, a small amount of calcite structure. Only the stratum corneum of the striatum and the stratum corneum of the river scorpion are with silica and a little impurity. The crystal structure, lattice constant and unit cell volume of ancient shells， it are not different from those of modern shells [8-13] Crystallography books and textbooks the conclusion record that the physical properties of the aragonite structure are unstable, after many years be converted into a calcite structure is incorrect. Moreover, China's Tibet, the Penghu Islands in Taiwan Province, and the Sicily in Italy produce aragonite gemstones (mainly aragonite structures) that have survived for hundreds of millions of years.
2. From the Corbicula maxima Prime shell pearl layer and prism layer buried in the ground for thousands of years, the aragonite structure has developed to a higher degree of crystallization - "single crystal", making the spectral line stronger, narrower and less ! It is even more impurity-free than modern shells, which means that the aragonite structuce grains are grow and more stable. Further reversing the conclusion that geological crystallography is unstable about the crystal structure of aragonite and will eventually become calcite. Because there are very few calcite lines, maybe even calcite turns into a aragonite!
   Shell sample thicker, better test results!
3. many modern shells has calcite structure as shown in the table 2, but the ancient shells basically have no calcite structure, It shows that after a long period of time, the calcite of the shell became aragonite.
4. The "shellfish science program" considers that the shellfish shell prism layer is a calcite structure [9-13] is wrong. It is confirmed from the above shells and ancient shells that the prism layer of the shell is all aragonite structure.
5. We studied the electron probe detection of 8 kinds of ancient shells and modern shell samples, and found

many voids - "Double Chen weathering hole CC" is shown in Table 5! We hope that it will become another way to apply ancient shells and even ancient artifacts to detect the age!

References

[1] Zhang Xi, Qi Zhongyan. The Outline of Shellfish [M]. Beijing: Science Press 1961.

[2] Sonjinjiayi. The canon of pearls. Beilong Pavilion, 1965.

[3] Xiaolinxinerlang, Dubuzheguang. Pearl Research [M], Xiong Daren Translation, Beijing Agricultural Press, 1966.

[4] Jiang liangjun, 1960. Mineralogy ii [M]. Beijing: metallurgical industry press.

[5] Rock ore research office, department of geology, nanjing university, 1978. Crystallography and mineralogy [M]. Beijing: geological press.

[6] Handbook of mineral X-ray powder crystal identification [M], guiyang institute of geochemistry, Chinese Academy of Sciences, 1978. Mineral X-ray powder crystal identification manual. Science press.

[7] Professor kwang-ming liu sunny's blog, http://blog.sina.com.cn/drgmliu.

[8] Chen Guiqing, Chen Junhao, Zhang Xiujun. The crystal structure of the *Pinctada maxima* shell, the. *Pinctada margaritifera* shell, the *Pinctada nigra* shell and the *Pinctada martensi* shell [J]. Marine Drug 1985, 4 (1): 20-22.

[9] Chen Junhao, Chen Guiqing. *Pteria* (Magnavicula) *penguin* shell, *Pinctada chemnitzi* shell, *Pinna atropurpurea* shell and *Perna viridis* shell crystal structure [J]. Marine Drug 1986, 5 (1): 20-23.

[10] Chen guiqing, Chen junhao, Chen piao. Study on the natural pearl and shell of *Pinctada martensi.* Marine Drug 1986, 5 (3): 4-7. In 1987, he was awarded "excellent paper award" by Marine drug.

[11] Chen guiqing, Chen junhao, 1988. Crystal structure type of shell [J]. Chinese Marine drug, 1-2: 21-29.

[12] Chen Guiqing, Chen Junhao. New conclusions about the crystal structure of pearls and shells. Applied Oceanographic Journal, Vol. 36, No. 4, Nov. 2017/11, P. 528-531.

[13] Chen junhao and Chen guiqing. Crystal structure and application of pearls and shellfish [M]. Jinan university press, December 2018.

[14] Cao boxun. AMS carbon C14 dating method and analysis. Baidu library - education - higher education - science. In 2014.

[15] Reshui redaction. Carbon -- dating and prehistoric archaeology in China [M]. The one they called bean mesh. 2013/7/22.