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Original Paper

A Cheap New Geological Dating Method Developed from Ancient Shells Study

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Abstract

The vast majority of researchers on ancient shells are biologists, who are not familiar with X-ray diffractometers, etc. We are physical chemists who use X-ray diffraction to observe the changes in the crystal structure of ancient shells? Then use WDX electron probe to observe the changes in the microstructure of ancient shells. After discovering shells for a long time, calcite turned into aragonite, overturning the conclusion recorded in geological crystallographic books that aragonite's structure and physical properties were unstable and would eventually transform into calcite. Unexpectedly discovered that the "Shuang chen Weathering Cave ***CC****" of ancient shells has changed over time, it can be used as a new method for geological dating.*

The use of carbon 14 (C14) isotope geological dating method is quite expensive and lacks accuracy, causing many jokes. The "Shuang chen Weathering Cave ***CC****" of ancient shells may be used as a new geological dating method, and it is quite cheap!*

Keywords

marine biology, aragonite structure, calcite structure, D/max-1-A type X-ray diffractometer, WDX electron probe, CC- double Chen weathering cave

Introduction

Authoritative textbooks in China: Zhang Xi and Qi Zhongyan's "Outline of Shellfish Studies" believe that the structure of shells can generally be divided into three layers, with the outermost layer called the stratum corneum, which is only composed of shell elements. The middle layer is a prism layer, which occupies the majority of the shell and is composed of angular columnar calcite (ca1cite). The inner layer is usually composed of leaf shaped aragonite, known as the pearl layer, which is glossy, and pearls are formed from the nacreous layer. This theory has been widely cited and has been read by almost all biology students in China.

In the 1980s, we used X-ray diffraction to prove that the conclusion that the shell prism layer is a calcite structure was completely incorrect, which may have been copied from the Japanese. However, shellfish expert Master Hu observed under a microscope and believed that it was still a calcite structure. Oh my goodness! In the 1920s, shellfish scientists still don't know that crystal structure can only be determined by X-ray diffraction. The German physicist Roentgen discovered X-rays on November 8, 1895!

In the 1980s, Huang Baoyu, a researcher at the Nanjing Institute of Paleontology, provided ancient shells: ***Schistodesmus*** **sp.,** ***Schistodesmus lampreyanus*** **(Baird & Adams),** ***Unio douglasiae Griffith*** **et Pidgeon,** and ***Lamprotula hazinic*** **(Heude)**. We use the electron microprobe from the South China Sea Institute of Oceanography, Chinese Academy of Sciences!

Recently, the ***Corbicula maxima Prime*** shell was borrowed from Tan Yehui, a researcher at the Chinese Academy of Sciences Guangzhou South China Sea Institute of Oceanography, and Dr. Chen Zhiyun, and excavated from the Longyan Village Water Conservancy Project in Shunde, Guangdong. Collectors: Zhao Huanting et al. Collection time: February 1961. Era: 500 to 1000 years ago. Measurement date/time: 2015-11-27 9:48:41. Using the Empyrean X-ray diffractometer from **Sun Yat Sen University**.

The first part

Comparison of X-ray diffraction lines between modern and ancient shells

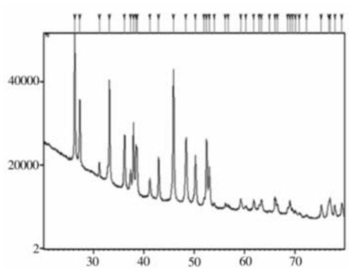
Grind each layer of the shell into powder using an agate mortar and pass it through a 360 mesh sieve. Using D/max-1-A X-ray diffractometer and Cu target K_{α}X-ray diffraction, under 40kV, 50mA conditions, within 30 minutes from 2θ Range 20^0-80^0, instrument uses a Plot plotter and automatically prints 2θ, Absolute strength I and corresponding crystal plane group spacing d. Refer the above results to the international universal phase analysis (JCPDS) card to determine the crystal structure of the sample.

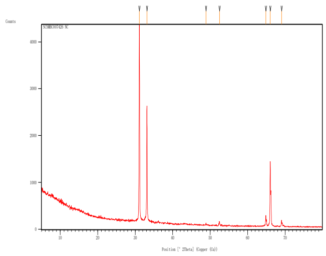
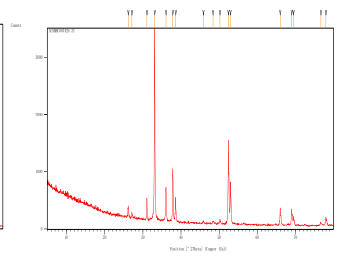
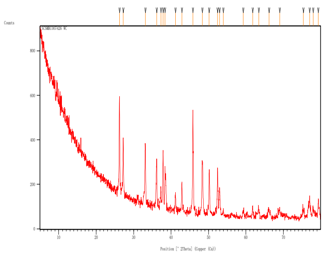
d=0.3399nm, and the horizontal bars at the bottom of the spectral lines are all aragonite structured spectral lines.

1. X-ray Diffraction Results

Table 1. X-ray Diffraction Data of Modern and Ancient Shells

Modern Cristaria plicata(Leach) Shell Powder		***Corbicula maxima* pearl layer**		***Corbicula maxima* prismatic layer**		***Corbicula maxima* periostracum layer**	
d(nm)	I/I_0 %	d (nm)	I/I_0 %	d(nm)	I/I_0 %	d(nm)	I/I_0 %
0.3399	99.99	0.2875	100.00	0.3407	5.31	0.3399	90.81
0.3276	51.05	0.2706	58.06	0.3287	2.61	0.3279	54.75
0.2875	11.22	0.1862	1.48	0.2879	10.97	0.2703	54.46
0.2705	79.03	0.1744	2.09	0.2709	100.00	0.2484	46.31
0.2487	41.80	0.1438	5.77	0.2492	16.96	0.2413	20.54
0.2412	16.49	0.1415	32.81	0.2378	27.43	0.2377	56.42
0.2376	53.68	0.1361	3.21	0.2334	13.13	0.2345	36.76
0.2342	37.09			0.1979	1.33	0.2193	16.07
0.2333	33.62			0.1881	1.45	0.2110	28.15
0.2192	14.26			0.1817	2.48	0.1980	100.00
0.2108	31.65			0.1747	42.95	0.1883	50.92
0.1980	100.00			0.1729	21.7	0.1819	41.6
0.1883	47.76					0.1746	46.3
0.1817	37.27						
0.1761	5.95						
0.1745	50.73						
0.1728	30.45						



X-ray diffraction pattern: Figure 1 *Modern Cristaria plicata (Leach) Shell Powder*. Figure 2 *Corbicula maxima* pearl layer.

Figure 3 *Corbicula maxima* prismatic layer. Figure 4 *Corbicula maxima* periostracum layer.

2. Discussion of Results

2.1

The crystal structure of ancient shells is the same as that of modern shells. The prismatic layer is all aragonite structure, which overturns the conclusion of "shellfish outline".

2.2

The X-ray diffraction pattern of the pearl layer in the ***Corbicula maxim*** shell appears very special, with the absolute intensity of the strongest spectral line d=0.2875nm reaching I=4290.7 (the maximum intensity of the spectral line in a typical shell is about 700). The spectral lines are very strong, narrow, and few, all of which are thick aragonite grains with obvious "monocrystallization" and no impurity spectral lines. Unlike geological crystallography think, where the structure of aragonite is unstable, it will eventually become calcite. But rather development towards a higher degree of single crystal indicates that the structure of aragonite is stable.

According to the **Scherrer** formula of X-ray diffraction theory of crystals, the strengthening, narrowing, and decreasing of spectral lines are caused by the growth and thickening of grains in this diffraction direction (preferential orientation growth), which we refer to as the "single crystal tendency".

The growth process of seashells is the growth process of aragonite crystals, constantly in an unbalanced state. Due to vacancies or impurities filling the lattice, the lattice distortion changes the spacing between crystal planes and broadens the spectral lines, resulting in new internal stresses. After the death of shellfish, crystal growth stops and no new internal stress is generated. The stress inside the shell gradually releases, vacancies are gradually filled or impurities are gradually eliminated to the grain boundary to eliminate internal stress. At this time, internal stress is also concentrated at the grain boundary, so this area is prone to weathering. The grains of aragonite continue to grow, therefore; Make the spectral lines stronger, narrower, and fewer!

Due to the ***Corbicula maxima*** shell, it is less affected by the surrounding soil, which better reflects this process.

2.3

The X-ray diffraction pattern of the prismatic layer of the *Corbicula maxim* shell is similar to that of the pearl layer, with strong, narrow, and few spectral lines. All spectral lines are thick aragonite grains with a “single crystal tendency”, and there are no impurity spectral lines.

The absolute intensity of the strongest spectral line d=0.2709nm reaches I=3406.33, which is very strong, narrow, and has very few spectral lines! But because the prism layer is located in the middle of the shell, between the nacre layer and the stratum corneum, the internal stress release is slower, so the spectral lines are slightly more than the nacre layer. It is exactly the same as the pearl layer. From its X-ray diffraction pattern, it appears that many weak spectral lines have become almost flattened and are developing towards a “monocrystalline trend”, similar to the pearl layer above, without impurity spectral lines.

2.4

X-ray diffraction pattern of periostracum layer of the *Corbicula maxim* shell. Due to the influence of the epidermis, the spectral lines become more numerous and wider. But all spectral lines are of aragonite structure and have no impurity spectral lines.

2.5

It can be seen from the table that there are more spectral lines in the shell of modern pleated clamshell than that of ancient clam shell. Especially from the spectrum diagram is clear at a glance. The aragonite structure of the ancient shell continues to grow, with obvious “monocrystalline”, excluding impurities. Modern shells contain some calcite, but ancient shells contain almost no calcite. It shows that after a long age of shells, calcite becomes aragonite!

The second part

Electron Microprobe experiment of four kinds of ancient shells

1. Materials and Methods

In the 1980s, researcher Huang Baoyu from the Nanjing Institute of Paleontology provided us with four types of ancient shells and explored them using the Electron Microprobe from the South China Sea Institute of Oceanography, Chinese Academy of Sciences!

2. Experimental Results

2.1

Schistodesmus sp.shell. 102 points, Ding Village, Xiangfen, Shanxi, with field number ADY201 1983/9/9. Era: hundreds to thousands of years.

Elements with atomic numbers below 11 (Na) cannot be measured, therefore; $CaCO_3$ can only be calculated from the CaO molecular formula. The results are shown in Table 1.

$CaO+CO_2$--→$CaCO_3$ $M_{CaCO3}=(100.089 \div 56.0794) \times M_{CaO}=1.784777 \times M_{CaO}$.

56.0794 100.0892

Inner layer $M_{CaCO3}=1.78478 \times 48.165=85.964$; Surface $M_{CaCO3}=1.78478 \times 45.125=80.538$. The same applies below.

Total in the table Σ The sum of calcium carbonate and other oxides. Sum of electron probe measurements of modern shells Σ. They are all around 100%, which is caused by errors caused by certain factors and can be normalized to 100%. However, the results of ancient shells are at a certain distance from 100%. This is the result of ancient shells weathering for thousands of years, and we define it as the **“Shuang Chen Weathering Cave”**: $CC=100-\Sigma$. The various parts of ancient shells are different, and the average value $\overline{CC}$ is taken to represent them. According to the dozens of modern shells we tested, the general result is $98.5<\Sigma$. Therefore, it is assumed that ***CC*** values below 2 can be ignored and considered as 0, indicating that there is no **“Shuang Chen Weathering Cave”**. Because the range of electron probe testing is very small, important data needs to be measured at several points to obtain the average value, the same below.

2.2

***Schistodesmus lampreyanus* (Baird & Adams) shell** 102 points, Ding Village, Xiangfen, Shanxi, 1986/12/16. Era: hundreds to thousands of years. The results are shown in Table 2.

2.3

***Unio douglasiae Griffith* et Pidgeon shell**. No.102, Dingcun, Xiangfen, Shanxi, with field number ADY201 1986/12/16. Era: hundreds to thousands of years. The results are shown in Table 3.

2.4

***Lamprotula hazinic* (Heude)** shell. 102 points in Ding Village, Xiangfen, Shanxi, with field number ADY193 1986/12/16. Era: hundreds to thousands of years. The results are shown in Table 4.

2.5

Modern *Pinctada Martensi* (Dunker) pearl shell. The results are shown in Table 5.

2.6

Modern *Lamprotula mansuyi* (Dautzenberg et Fischer) shell. The results are shown in Table 6.

2.7

Modern *Mactra Antiquata Spengler* shell. The results are shown in Table 7.

2.8

Modern *Arca (Anadara) granosa Linnaeus* shell. The results are shown in Table 8.

Table 1-8. Oxide of Shell

Oxide	Na_2O	K_2O	Fe_2O_3	MnO	SiO_2	MgO	TiO_2	Al_2O_3	CaO	$CaCO_3$	Σ	*CC*	*CC*
Table 1 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
Table 2 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	
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	19.9
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	
Table 3 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	
Table 4 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	
Table 5 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	
Prismatic layer	0.429	0.023	0.039	0.000	0.000	0.085	0	0.065	55.670	99.360	100.000	0	0
Periostracum	0.282	0.039	0.000	0.000	0.019	1.205	0	0.048	55.137	98.409	100.000	0	
Table 6 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	
Prismatic layer	0.59	0.09	0.06	0.11	0.43	0.05	0	0.12	55.67	99.359	100.809	0	0
Periostracum	0.25	0.00	0.00	0.04	0.42	0.03	0	0.08	55.38	98.841	99.661	0	
Table 7 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	
Table 8 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 9. Comparison of the "Double Chen Weathered Hole *CC*" Result between Ancient and Modern Shells

Ancient shell species	**Oxide summation Σ**	**Double Chen weathered hole *CC***	**Moder shell species**	**Oxide summation Σ**	**Double Chen weathered hole *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

3. Result Discussion

3.1

We studied the electron probe Electron Microprobe detection of 8 samples from 4 ancient and 4 modern shells. As a result, many voids were found in the ancient shell-"Shuang chen Weathering Cave ***CC***" as shown in Table 9! We hope it can become a cheap method for dating ancient artifacts!

3.2

In order to achieve the purpose of this article, we sincerely hope that relevant researchers can conduct further research!

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90 year old commemorative works IV

Fund project "Artificial growth of aragonite crystals and artificial development of pearls"

Chen Guiqing, Chen Junhao 1985 (Approval No. 85084).

Fund project "Research on the Structure and Imaging Mechanism of Artificial Pearl Cores and Artistic Pearl Images"

Chen Guiqing, Chen Junhao. 1989 (Approval number 38870643).

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