Feigl's Solution: A Test for the Chemical Basis of Changes in the Strontium-Calcium Ratio in Fish Otoliths

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(Received November 24, 1995)

Key words: otolith, strontium, calcium, silver, manganese, Feigl's solution, proton microprobe

When sections of the otoliths of fish are scanned with a proton microprobe the ratio of strontium to calcium (continuous point-to-point measurements in cpm) changes from point-to-point.1) Observed over a sequence of observations, the changes in the Sr/Ca ratio often show underlying cyclic trends2,3) that can be recognized against background noise. Mugiya and Satoh4) reported observations of changes in the Sr/Ca ratio that were consistent with earlier observations that Sr levels were generally lower in the slower growing parts of the otolith. Mugiya and Satoh4) argue that their observations will be useful in delineating daily microincrements in fish otoliths, which, at present, is sometimes difficult to do. Before Mugiya and Satoh's4) method can be used it is necessary to clarify whether the observed change in Ca is a chemical event, i.e. a real decrease in local calcium concentration in the aragonite/strontianite solid state solutions5) of the otolith; or a measurement artifact caused, for example, by changes in otolith porosity. One possible test of whether the Ca variation is real is by staining the otolith with Feigl's solution.

A variety of staining methods have been developed to identify carbonate minerals by differential staining of mineral components.6) These methods are no longer used as more sophisticated spectroscopic methods have become available. However, one of the staining methods developed to distinguish between calcite and aragonite is Feigl's solution that relies on the difference in solubility between these otherwise chemically identical minerals. Solubility in mildly alkaline conditions generates OH ions that lead to the following sets of reactions:7)

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\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaCO}_3^- \\
\text{CaCO}_3 & \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \\
\text{CO}_3^{2-} + 2\text{H}_2\text{O} & \rightarrow \text{H}_2\text{CO}_3 + 2\text{OH}^- \\
\text{Mn}^{2+} + 2\text{Ag}^+ + 4\text{OH}^- & \rightarrow \text{MnO}_2 \downarrow + 2\text{Ag} \downarrow + 2\text{H}_2\text{O}
\end{align*}
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The characteristic gray color that results from application of Feigl's solution to calcium carbonates is caused by the mixed MnO_2 and Ag deposits. Feigl's solution was made up using the formula of Cheetham et al.8) A sagittal otolith of Pagrus (Chrysophrys) auratus (Sparidae) was sectioned in the dorso-ventral plane through the nucleus at right angles to the sulcus. The otolith section was exposed to Feigl's solution for 5 minutes causing visible blackening of the surface. The otolith section was patted dry and scanned9) with a proton microprobe in 8 parallel rows of 34 sample points 70 µm apart roughly centered on the nucleus of the otolith. A second scan of 100 points 70 µm apart was made along the dorso-ventral axis of the otolith also roughly centered on the nucleus of the otolith.

Treatment of otolith sections with Feigl’s solution results in the deposition of MnO_2 and Ag on the otolith surface. Scanning the stained otolith surface with the proton microprobe produces measurements (in cpm) of deposited Mn and Ag as well as the Sr and Ca that occur naturally in the otolith. Changes in Mn, Ag, Sr and Ca by sample point along the second (100 point) trace are shown in Figs. 1a, b, c, d, e. Silver (Ag) deposition was out of phase with Mn deposition (Fig. 1a). Manganese (Mn) deposition was in phase with Ca (Fig. 1b), but Sr was out of phase with Mn (Fig. 1c). Both Ag (Fig. 1d) and Sr (Fig. 1e) were out of phase with Ca. Statistically the correlations between elements (measured in cpm) were: Ag/Mn, r^2=0.20 (second order polynomial); Mn/Ca, r^2=0.8 (linear); Sr/Mn, r^2=0.59 (second order polynomial); Ag/Ca, r^2=0.35 (second order polynomial); Sr/Ca, r^2=0.37 (second order polynomial). The patterns in the 100 point traces can be more readily seen in the plots of the smoothed (5 pass median smooth) parallel scan data plotted in Fig. 2 as a surface plot.

The traces of Ca cpm along the growth axes of all otoliths showed changes in Ca. The amount of change involved was fairly high, ranging from 5 to 20% of mean Ca. How can this happen in an apparently solid crystalline aragonite otolith? The reaction of the otolith with Feigl's solution shows that both Sr and Ca variation is a chemical effect due to local changes in Sr and Ca concentration, not a measurement effect (e.g. due to porosity) for the following reasons. The solubility product of CaCO_3 is an order of magnitude greater than that of SrCO_3 (0.87 x 10^-8 mol. 1^-1 c.f. 1.6 x 10^-9 mol. 1^-1 at 25°C). Increasing SrCO_3 concentration in the aragonite/strontianite solid state solution10) decreases the amount of [OH^-] available for the reaction with Feigl's solution. In addition, because of the lower solubility of SrCO_3, the enthalpy of formation of...
Fig. 1. Different combinations of element cpm values plotted against sample number: a, Ag/Mn; b, Mn/Ca; c, Sr/Mn; d, Ag/Ca; e, Sr/Ca.

Fig. 2. Smoothed element cpm values (vertical axis) plotted against sample number (left horizontal axis) and scan number (right horizontal axis). Low values are light shaded, high values are dark shaded.

MnO₂ is higher than that of Ag⁺ (−124 K cal. mol⁻¹ for MnO₂ and +25.31 K cal. mol⁻¹ for Ag⁺) so that Ag⁺ precipitation will be favored at lower [OH⁻]. Therefore Ag⁺ precipitation should be greater with higher SrCO₃ concentration, and MnO₂ precipitation should be greater with higher CaCO₃ concentration. The traces show Ag cpm in phase with Sr cpm, and Mn cpm in phase with Ca cpm, as their chemistry predicts.

Why there should be changes in Ca concentration in the otolith is not known, but staining with Feigl’s solution shows that such changes are chemical effects. Consequently, the method of Mugiya and Satoh⁴ is a valid technique for the definition of otolith daily microincrements based on the difference in concentration of Ca between the light (mineral rich) and dark (matrix rich) zones that together comprise a microincrement.

This research was supported by MAFFish (New Zealand) IGNS (New Zealand) and HIGP (Hawaii). This is SOEST contribution No. 4262 and HIGP contribution No. 933.

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