

INTRODUCTION

In 1948, Wickman proposed that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater should increase as a function of time due to the decay of ^{87}Rb in the crust. At that time, due to an overestimation of the Rb/Sr ratio in the crust, Wickman concluded that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater should exhibit a monotonic increase of approximately 30% in 3600 Ma. The acquisition of more geochemical data pertaining to the crustal Rb/Sr ratio suggested that a far smaller increase in the seawater Sr isotopic composition was to be expected (less than 2%). This conclusion, along with the inability to resolve the fine scale isotopic variations observed in seawater, tabled the matter of the Sr isotopic evolution of seawater for many years.

The ability to resolve isotopic variations of less than 1-2 parts in 10^4 coincided with the development of the Apollo program. Larger data sets, real-time data acquisition and ultraclean microchemical procedures were required to extract the lunar chronology from lunar rocks whose radiogenic enrichments were small. Temporal variations in the Sr isotopic evolution of seawater could now be approached.

Peterman et al. (1970) analyzed 25 samples of carbonate shell material in order to study the Phanerozoic evolution of Sr in seawater. Rather than confirming the monotonic increase in $^{87}\text{Sr}/^{86}\text{Sr}$ as a function of time predicted by Wickman, they demonstrated that the Sr isotopic evolution of seawater contained several maxima and minima which were explained by interplays between volcanic episodes and the epeirogenic movement of continents on a global scale. Subsequent analyses of marine carbonates (Veizer and Compston, 1974) substantiated these findings.

In 1978, Faure et al. used their own analyses plus those from the literature to produce the most complete seawater Sr evolution curve at that time.

Burke et al. (1982) and Koepnick et al. (1985) have provided the geoscientific community with the most rigorous investigation of the Sr isotopic evolution of seawater to date. Their curve is defined by 786 Phanerozoic marine carbonates and phosphates. Isotopic resolutions of 4 parts in 10^5 demonstrate the existence of many more episodes of increasing/decreasing Sr isotopic values during the Phanerozoic. Detailed investigations of various portions of their curve by other researchers have substantiated their results (see LITERATURE REVIEW section and references therein).

Our research (Hurst and Davis, 1980; Hurst et al., 1985; Hurst, 1986a, 1986b) has focused on the practical applications of the seawater Sr evolution curve. To this end, we are compiling our own data while attempting to calibrate the data from other laboratories in order to produce the "best fit" seawater Sr evolution curve. The current state of our knowledge is presented in this short course.

METHODOLOGY

The analytical techniques which we employ are based upon ultra-clean, microchemical methods. In contrast to the numerous authors cited in the INTRODUCTION, much of our work involves the Sr isotopic analysis of pristine carbonate cements, concretions and laminations. Fossil material is used when available although it is not mandatory. Our main concern is to provide a technique which can be used as an isotopic chronometer and evaluate interbasin correlations. We refer

to our technique as the Sr isotopic chronostratigraphic method (SICM).

The extraction of soluble carbonate by acid leaching is not a trivial matter since radiogenic Sr can be removed from other mineral phases which may be present (e.g. clays). Thus the choice of acid is dependent upon the lithology. Both dilute acetic (clay-rich lithology) and 0.1N HCl (clay-absent to clay-poor lithology) are routinely utilized. In our experience with detrital-rich shales containing less than 2% carbonate, the Sr isotopic compositions of the acetic versus 0.1N HCl leachates are identical within analytical limits. This was not the case when more concentrated acids were used to leach the sample. In addition we never heat the sample for fear of removing weakly bound Sr. These techniques have been developed and refined over the last seven years. In addition to the chemical techniques, we have used XRD analyses to examine the effect of the acids on different lithologic types and we continue to use it in new situations. Once a sample is leached, the leachate is filtered, dried and Sr is separated using standard ion exchange techniques.

Our mass spectrometric techniques begin by loading 300ng to 1 ug of Sr on a rhenium filament with a Ta_2O_5 substrate. Instrument fractionation is corrected by normalizing the $^{86}Sr/^{88}Sr$ ratio to its accepted value of 0.11940. Generally 150-300 $^{87}Sr/^{86}Sr$ ratios are measured depending on the level of precision required. To quote Aristotle:

"It is the mark of an instructed mind to rest satisfied with the degree of precision which the nature of the subject permits and not to seek an exactness where only an approximation of the truth is possible."

Once the average $^{87}Sr/^{86}Sr$ ratio is obtained, the analysis is

corrected relative to the NBS SRM 987 Sr isotopic standard. Our certified value for this standard's $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.71014. Since 1980, our measured value of this standard has ranged from 0.71012 to 0.71022 (average 0.71018 ± 0.00001). We typically analyze this standard one to two times a month. Hence if our current measurement of the standard is 0.71017, we subtract 0.00003 from each sample analysis to correct for the NBS SRM 987 standard. In this way, as more precise and accurate measurements of the standard are made, the data generated by our laboratory is biased in a systematic way and can be corrected. Unfortunately, this is not the approach of all laboratories, making the incorporation of their data difficult.