

Ross Sea ^{226}Ra and Ba profiles measured by MC-ICP-MS.

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The measurement of ^{226}Ra in seawater has several potential applications in oceanography, particularly as a tracer of water masses and of groundwater input into the oceans (Moore, 1996). $^{226}\text{Ra}/\text{Ba}$ also shows potential for dating marine carbonates, but the seawater $^{226}\text{Ra}/\text{Ba}$ ratio must be known. The majority of work on ^{226}Ra in seawater has used radio decay methods such as alpha scintillation, but the poor efficiencies of radiation counters limit the precision of these measurements to about 5% (Chung, 1980), and requires a sample size of at least 20 litres. Atom counting methods such as mass spectrometry significantly reduce these limitations. Thermal Ionisation Mass Spectrometry (TIMS) has an uncertainty < 2% and requires only 40ml. However, TIMS analysis is time consuming and can be subject to organic interferences. We have developed and tested the use of multiple ion counting ICP-MS to analyse ^{226}Ra on seawater samples using a Nu instrument. We describe the potential and limitations of this approach and demonstrate that 2% (2 σ) uncertainty can be achieved on 120ml of seawater. Backgrounds across the Ra mass range are very low (<1cps) when using clean cones, but molecular interferences of ~100 cps appear on several masses if the cones are contaminated with Ba. This problem necessitates the chemical separation of Ra from Ba prior to analysis. Nevertheless, MC-ICP-MS is significantly less time consuming than TIMS.

Three water column profiles from the Ross Sea and Southern Ocean have been measured in order to assess the variability of $^{226}\text{Ra}/\text{Ba}$ in the Ross Sea and the open ocean. We measure a surface water ^{226}Ra concentration of 0.386 ± 0.014 fmol $^{226}\text{Ra}/\text{kg}$ in agreement with a value of 0.386 ± 0.0048 fmol $^{226}\text{Ra}/\text{kg}$ from the same sample analysed independently using TIMS. ^{226}Ra concentrations are relatively constant with depth, and are close to those in the open Southern Ocean measured at GEOSECS station 287 (Chung, 1980). Ross Sea $^{226}\text{Ra}/\text{Ba}$ ratios are also within error of those measured at station 287 (4.9×10^{-9} mol/mol). This similarity indicated that there is minimal discharge of ^{226}Ra into the Ross Sea, either by surface weathering or by groundwater discharge – a reassuring result for the use of Ra/Ba dating of carbonates in the area.

References

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Experimental determination of the stability of aluminum-borate complexes in hydrothermal solutions

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Boric acid is an important component of granite-derived fluids and thermal waters whose concentration, as measured in fluid inclusions, may reach 30 Wt% (Peretyazhko et al., 2000). To check for the formation of Al-borate species, similar to aqueous Al-silicates, a series of experiments was performed including a ^{27}Al NMR spectroscopy study at 25°C, and gibbsite and boehmite solubility measurements from 50 to 200°C. ^{27}Al spectra performed at pH=9 in Al-B solution with $m(\text{B})=0.02$ show the presence of two peaks at 80.5 and 74.5 ppm which correspond to $\text{Al}(\text{OH})_4^-$ and a single Al-substituted Q_{Al}^1 dimer, respectively. When $m(\text{B})=0.02$, a third peak appears at 69.5 ppm which can be assigned to the Q_{Al}^2 trimer. The observed chemical shifts are close to those of the Al-Si dimer and trimer (74 and 69.5 ppm, respectively; Pokrovski et al., 1998) which demonstrates the chemical similarity of Al-B and Al-Si complexes. Gibbsite and boehmite solubility was measured in weakly basic solutions as a function of boric acid concentration. Equilibrium solubility was reached within several days at $m(\text{B})=0.01-0.1$, but Al concentration increased continuously at $m(\text{B})=0.2$ due to the formation of Al-polyborates. The constant of the reaction $\text{Al}(\text{OH})_4^- + \text{B}(\text{OH})_3^0_{(\text{aq})} = \text{Al}(\text{OH})_3\text{OB}(\text{OH})_2^- + \text{H}_2\text{O}$ decreases very slowly with increasing temperature to 200°C. The log K values deduced from the solubility measurements in $\leq 0.1\text{m}$ H_3BO_3 solutions are 1.58 ± 0.10 , 1.50 ± 0.15 , 1.50 ± 0.20 , and 1.25 ± 0.10 at 50, 78, 150, and 200°C, respectively. These results demonstrate that in a solution containing ~0.5g/l of boron at 400°C and 0.5 kbar, $\text{Al}(\text{OH})_3\text{OB}(\text{OH})_2^-$ accounts for ~50% of total aluminum. At boron concentration >1g/l the formation of Al-polyborates may considerably increase aluminum transport capacity of hydrothermal fluids. *This study was supported by CNRS and RFBR (grant 01-05-64675 to BT).*

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