8. Radium studies in the Crozet region

Paul Morris, Peter Statham, Ian Slater, Gary Fones

Background

In order to estimate the time since water bodies were last in contact with bottom sediments (T_w), and thus proposed benthic Fe source, we will use an approach based on the ratio of ^{223}Ra/^{228}Ra at the Crozet shelf relative to that found in a given water parcel:

$$\left[\frac{^{223}Ra}{ex^{228}Ra}\right]_{obs} = \left[\frac{^{223}Ra}{ex^{228}Ra}\right]_{i} e^{-\lambda_{223}T_w}$$

where $\left[^{223}Ra/ex^{228}Ra\right]_i$ is the activity ratio at the coastline and $\left[^{223}Ra/ex^{228}Ra\right]_{obs}$ is the activity ratio in the samples. This method is based on the decay rate of ^{223}Ra relative to ^{228}Ra, which corrects for mixing effects. Since the open ocean contains measurable activities of ^{228}Ra (but relatively little ^{223}Ra), we normalize ^{223}Ra to ex^{228}Ra which is simply the observed activity minus the oceanic end-member. Therefore measurements of natural series Radium isotopes will give information on time since water was in contact with Ra source (sediments, ground-waters, run off), and if all necessary isotopes measured also an estimate of dilution. The work is being done in collaboration with Dr Matt Charette at WHOI.

Main objectives of study

- To study Fe surface distributions in relation to radium, with Ra acting as a proxy of water that has been in contact with sediments or other Ra sources
- In a vertical profile to use Ra data as indicator of upwelled benthic waters (in contact with sediments) and to measure Fe in relation to this Ra
- To provide information on the physical turbulence and upwelling in the vertical profile

Sampling Rationale

Surface underway - Surface water Ra samples (~150-400 L) for Ra samples were originally collected using the ship's fire hose system, this approach worked well until the water tanks were switched and contamination was found in the samples. Sampling was then switched to the ships non-toxic supply (after Ra 68 onwards) and filtered through a 10 μm and 1 μm pre-filter. 200 litre barrels were filled for sampling (Fig. 1); two barrels were used when the sample was anticipated to be low in Ra. The water was also sub-sampled for ancillary measurements (i.e. salinity, nutrients). The water was then passed through MnO_2-impregnated fibres to collect the Ra isotopes. During D285, 72 surface radium samples (plus one sample for Actinium) were collected, while on D286, 38 surface samples were collected including a transect from Port Elizabeth to out past the shelf. The sampling track can be seen in Fig. 8.1, with the triangles representing D285 samples and the diamonds D286.

Specific targets for D285 were horizontal transects across clear gradients in biological activity and water types. In particular from J to M3, from M3 to M5, at M6 (as typical HNLC water with minimal Ra activity anticipated) and along the Sea-Soar transect to the north of the Crozet

plateau. Surface sampling for D286 concentrated on repeating samples to the south of the islands around M6, presumed to be HNLC and out east towards the sediment sampling site at M5. Further emphasis was placed on surface sampling a transect through the islands.

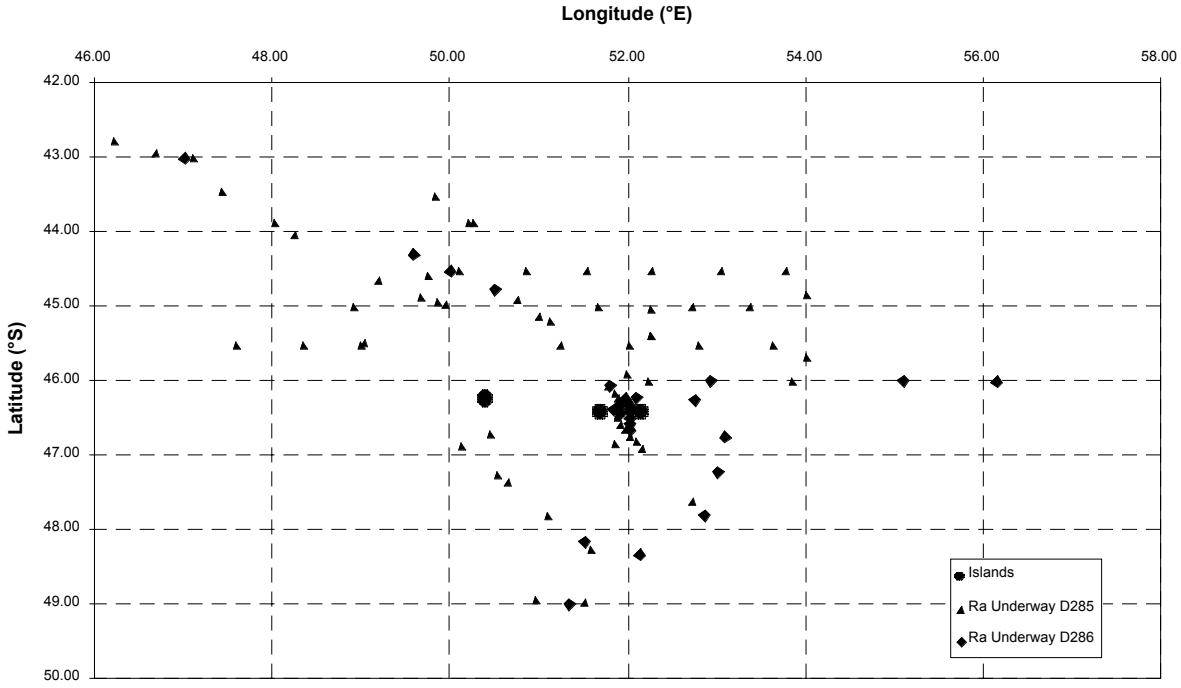

Fig. 8.1 Radium underway sampling track

Table 8.1 M3 sampling for Radium samples – 9 depths in total

Sample ID	Julian day	Date	Lat	Long	Depth (m
Ra 57	330	25/11/2004	46.073	51.766	50
Ra 134	12	12/01/2005	46.042	51.961	100
Ra 31	323	18/11/2004	46.024	51.809	150
Ra 106	358	23/12/2005	46.082	51.783	300
Ra 111	366	31/12/2005	46.062	51.777	500
Ra 9	318	13/11/2004	46.057	51.792	900
Ra 113	366	31/12/2005	46.046	51.774	1687
Ra 112	366	31/12/2005	46.045	51.775	1877
Ra 105	357	22/12/2005	46.069	51.777	1930

CTD Samples – Samples for Radium analysis were also collected opportunistically from the ThCTD casts. Major scientific rationale was to build up a profile at M3 with repeat visits over the two cruises. CTD samples were also taken at other stations at various depths to determine benthic input, the emphasis was on collecting samples at 150m. In total 21 CTD radium samples

were taken, 9 from D285 and 12 from D286. The repeat station of M3 was sampled in total 9 times to compare with the mesh bags on the M3 mooring. Table 8.1 gives the sample data for CTD radium samples for the M3 repeat station. Table 8.2 gives the data for the other CTD samples.

Sampling of the CTD involved the firing of up to 15 Niskin bottles (20 L) on the stainless steel CTD at the depth of interest. On recovery the Niskins were emptied into 25 litre carbuoys and carried round to the radium barrels and emptied. Normal Ra procedures were then undertaken including the sub-sampling of salts and nutrients along with the filtering of the sample through the MnO_2-impregnated fibres.

Table 8.2 CTD sampling for Radium samples – 12 Samples in total

Sample ID	Julian day	Date	Station ID	Lat	Long	Depth (m)
Ra 101	357	07:51:00	15566	46.370	51.827	85
Ra 46	325	20/11/2004	15503	47.796	52.855	150
Ra 65	332	27/11/2004	15523	45.506	48.986	150
Ra 69	335	30/11/2004	15533	44.950	49.961	150
Ra 78	338	03/12/2004	15542	43.117	47.185	150
Ra104	357	22/12/2004	15570	46.263	51.957	150
Ra109	362	27/12/2004	15580	45.998	56.151	150
Ra 96	355	20/12/2004	M10	44.518	49.991	150
Ra 93	354	19/12/2004	M9	42.994	47.026	150
Ra 97	356	21/12/2004	M10	44.510	49.967	900
Ra 8	316	11/11/2004	M4-1	43.927	50.257	1000
Ra 49	328	23/11/2004	M6	49.016	51.473	1000

Table 8.3 M3 physical mooring depths for Ra mesh bags sampling – 11 depths in total

Ra Array Bag No.	Depth	Date In	Time In	Date Out	Time Out
1	50	13/11/04	05.50	09/01/05	8.55
2	100	13/11/04	05.55	09/01/05	9.00
3	150	13/11/04	06.00	09/01/05	9.05
4	200	13/11/04	06.05	09/01/05	9.10
5	300	13/11/04	06.10	09/01/05	9.15
6, 7	500	13/11/04	06.40	09/01/05	13.00
8	904	13/11/04	06.55	09/01/05	13.00
9	1307	13/11/04	07.10	09/01/05	13.20
10	1687	13/11/04	07.25	09/01/05	13.35
11	1877	13/11/04	07.35	09/01/05	13.45
12	1930	13/11/04	07.45	09/01/05	13.45

M3 Mooring – Mesh bags containing MnO_2-impregnated fibres were attached at different depths on the physical instrument mooring at M3 which was deployed during D285. The mooring was deployed on November 13th 2004 (JDay 318) and recovered on January 9th 2005 (JDay 9). The isotope ratio information obtained should give data on age of water since in contact with sediments.

Crozet Island sampling – Three samples were also taken during a field expedition to sample on the Crozex Islands. Sampling took place on Ile de la Possession on January 8th 2005. Samples were taken at a fresh water source (Fig. 3), in the surf zone and a few hundred meters offshore from a RIB, as well as a sample taken on board using the non-toxic. The fresh water sample was filtered at the sampling site at the Baie du Sphynx (Fig. 4). This transect will hopefully give a better indication of Ra input and dilution and thus potential Fe input from Crozet to surrounding waters.

Fig. 8.2 Field sampling for Radium

Fig. 8.3 Field filtration for Radium

Table 8.4 Sampling locations for Crozet Island Ra sampling

Sample ID	Date	Julian Day	Location	Lat	Long
Ra 131	08/01/05	8	Baie du Sphynx	46.414	51.866
Ra 132	08/01/05	8	Port Alfred	46.426	51.862
Ra 134	08/01/05	8	Mid-way	46.427	51.868
Ra 130	08/01/05	8	Discovery	46.425	51.906

Radium analysis

On-board ship – Because of the short half lives of Ra 223 and Ra 224 (^{224}Ra–$t_{1/2}$ = 3.66 days, and ^{223}Ra–$t_{1/2}$ = 11.4 days), it is essential to measure their activity on the ship. Four delayed coincidence alpha counting systems (Fig. 8.4) were provided by WHOI, for determination of gaseous Rn daughters of the Ra isotopes of interest, this allowed location of radium gradients in near real-time and subsequent adjustment of the sampling plan. Samples were rinsed four times with Ra-free Q-water and then dried using compressed air. The detectors were run for three hours or until the Radon^{219} counts reached 100. After two weeks the samples were then run for a second time for quantifying the supported activities of ^{223}Ra and ^{224}Ra from their parent radio-nuclides ^{227}Th and ^{228}Th.

At WHOI – In collaboration with Dr Matt Charette at Woods Hole Oceanographic Institution, USA, Radium isotopes will be counted non-destructively using gamma spectrometers and alpha scintillation techniques at WHOI during the summer of 2005. Samples that have not all ready been counted a second time will be analysed at WHOI for ^{223}Ra and ^{224}Ra, The Mn-fibres will then be ashed and ^{226}Ra and ^{228}Ra (^{226}Ra–$t_{1/2}$ = 1600 years, ^{228}Ra–$t_{1/2}$ = 5.75 years) counted on a well-type germanium gamma spectrometer.

Fig. 8.4 Delayed Incidence Counters on board

Data quality and provisional results

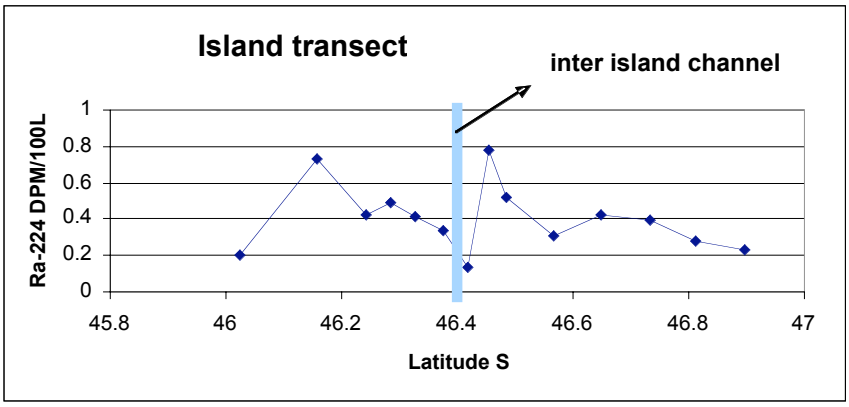

Fig8.5 Ra-224 activity along the N-S transect between the main Crozet islands

Data quality – Problems were encountered with the ships fire hose system and certain samples were contaminated. These were mainly to the south of the islands during D285, after switching to the ships non-toxic supply no further contamination was noted. These samples will be checked and rejected for the final work undertaken at WHOI. All samples from D285 were measured twice on board ship along with all the samples from D286 being measured once. The priority is for the equipment and samples to be air freighted back to WHOI so the second counts can be undertaken on the remaining D286 samples. Subsequently samples will be prioritized for the ^{226}Ra and ^{228}Ra analysis at WHOI.

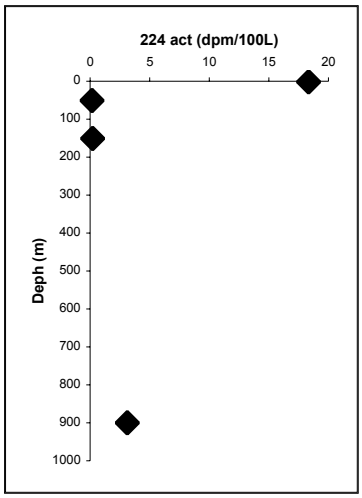

Fig. 8.6 Provisional 224 act plot for M3

Provisional results – Age models require a good end-member, source 224/223 ratio, and as this had not been determined at the end of leg 1, corrected Ra-224 counts are plotted in Fig. 8.5 showing data on the transect between the main islands on the Crozet plateau (Ile de la Possession and Ile de l'Est).

Higher activities are evident around the islands but a clear trend is not evident with distance inferring multiple sources and complex mixing in this zone. A provisional data plot for CTD radium samples from M3 indicate a high surface Radium224 signal potentially meaning a relatively new source of water recently in contact with sediment or rock. Interestingly at 900m there is also a signal indicating a potential benthic or deep source of radium.