ESR analysis of fluorescence band in corals

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Coral cores can provide a continuous record of the marine environment spanning over several hundred years. Using a variety of isotopic techniques it is possible to reconstruct palaeoclimates (e.g. Gagan *et al.* 1994, 1998; McCulloch *et al.* 1994, 1996, 1999) as well as environmental changes such as palaeofloods (Tudhope *et al.* 1995). One of the most interesting characteristics of coral sections from inshore regions is the occurrence of fluorescence bands. Some authors have attributed these to terrestrial fluvial discharge, where the corals incorporate humic substances during flood events. As a consequence, it was anticipated that sulfur-bearing components would generate the fluorescence (Isdale 1984). Others have argued that fluorescence bands are due to density changes resulting from stress from the low salinity flood plumes (Barnes and Taylor 1998).

Ikeda *et al.* (1992) measured an ESR scan on a 15 year slice of a coral from the Great Barrier reef. ESR measurements were carried out with a pin-hole cavity every 1 mm. The ESR spectra showed two main lines, those at g=2.0031 and g=2.0007 which have been attributed to SO_3^- and CO_2^-, respectively (Debuyst *et al.* 1990, 1991, Barabas 1992, Barabas *et al.* 1992a,b). Ikeda *et al.* (1992) showed with doping experiments that the intensity of the ESR line at g=2.0031 increases with the amount of SO_3^{2-} in aragonite, but was independent of SO_4^{2-}. Ikeda *et al.* (1992) also found a direct relationship between fluorescence bands and the intensity of g=2.0031 whilst intensity changes of g=2.0007 were attributed to differences in the density of the coral. In the ESR scan (Figure 2 of Ikeda *et al.* 1992), the signal at g=2.0007 showed more pronounced peaks than the signal at g=2.0031. Most of the peaks in the scan of the two signals were related, however, some larger peaks in the signal intensity of g=2.0007 were not reflected in the scan of g=2.0031.

In order to address the question whether fluorescence bands were attributable to increased sulfuric contents or density, we chose a coral core from Pandora Reef collected in late 1998. This section of the Great Barrier Reef is reached by the annual flood plumes discharged from the Burdekin River. A 1 cm thick slice was cut from the core which was exposed to UV light to identify the fluorescence bands (Figure 1). Rather than producing a continuous ESR scan, which would make it difficult to distinguish between fluorescence and density, samples were extracted for conventional ESR measurements. Four different fluorescence bands were chosen, three wide ones (1983 (A), 1974 (D) and 1968 (J)) and one rather thin one from the drought of 1969 (G). For comparison, additional samples were extracted from the non-fluorescent coral immediately above and below the fluorescence bands. Samples were drilled with a computerised high precision mill (Gagan *et al.* 1994, Alibert and McCulloch 1997). Sample weights varied between 27 and 51 mg.

For the measurement of the ESR signals at g=2.0031 and g=2.0007, the samples were irradiated with 5 kGy. Measurements were carried out at 2 and 100 mW. The signal at g=2.0057, which has been attributed to SO_2^- (Barabas 1992), can be measured after thermal activation (Brumby and Yoshida 1994, Martinez Walter 1994,Yoshida and Brumby 1999). Prior to the measurement of g=2.0057, the samples were heated for 7h at 150 °C. The ESR spectra are shown in Figure 2. However, as can be seen in Figure 2A, the irradiated, non-heated corals also show a small signal at g=2.0057.

Figure 3 shows the intensity measurements of all signals in all samples (normalised on weight). If fluorescence was related to SO_2^- (g=2.0057) or SO_3^- (g=2.0031), the respective signal intensities of samples A, D, G and J would be higher than either of the two surrounding ones. Figure 3 and Table 1 show clearly that this is not the case. The signal at g=2.0057 shows some relationship with the fluorescence bands before heating. However, the very small signal intensities

made quantitative analysis very uncertain and the variations seem within the statistical uncertainty of the ESR measurement. Note that just by chance, signals of approximately the same intensity would yield one to two «Y's» in Table 1.

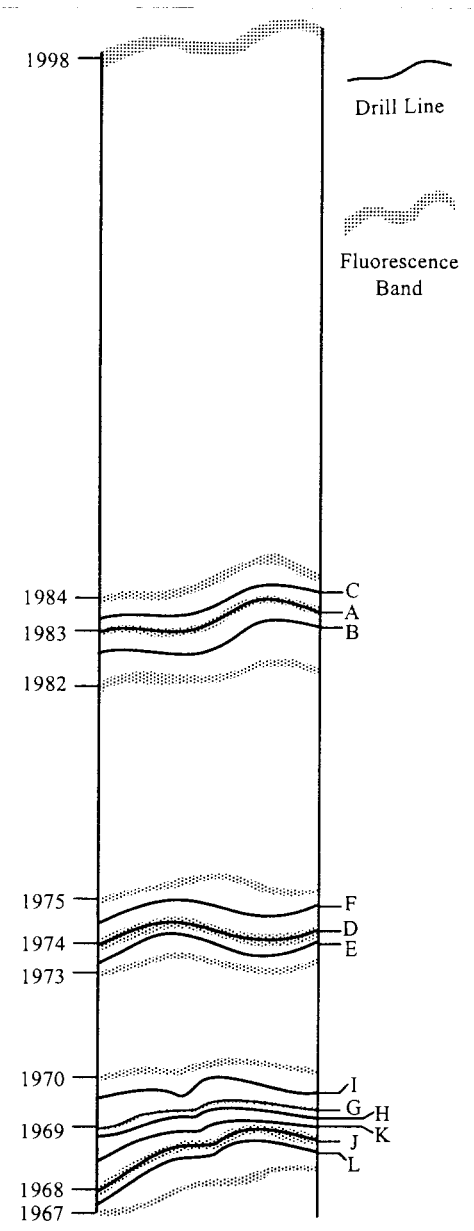

Figure 1.
Coral section from the Pandora Reef spanning 32 years between 1967 and 1998.

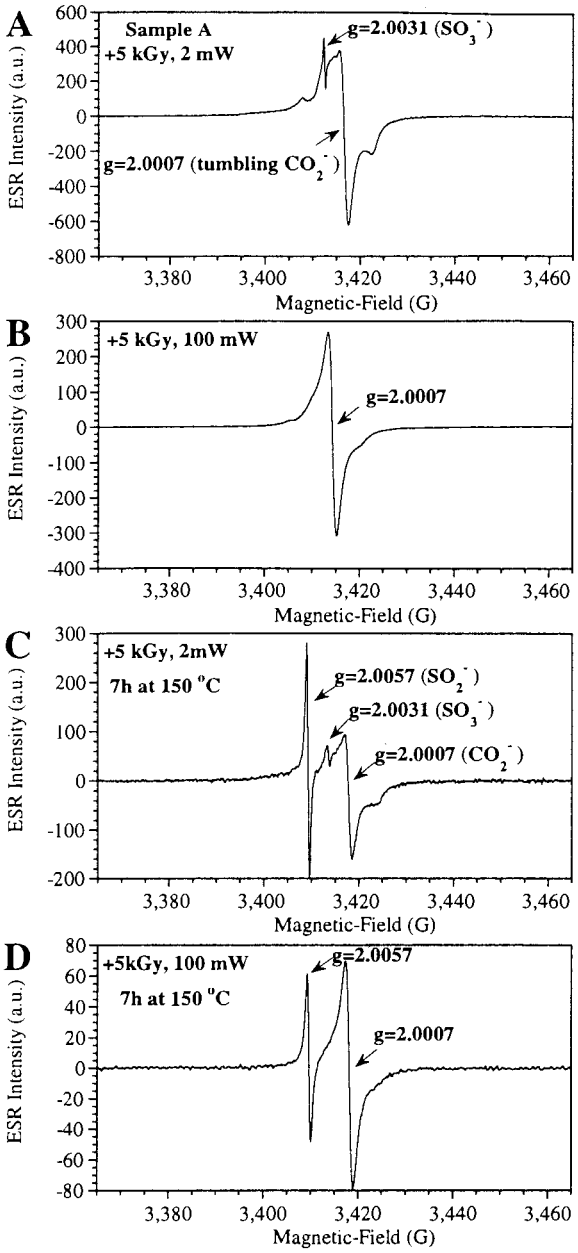

Figure 2.
ESR spectra

For three out of four sets, the intensity of g=2.0007 is related to the fluorescence band. These peaks are also by far the most pronounced ones, similar to the finding of Ikeda *et al.* (1992). Because it is thought that the signal at g=2.0007 is a surface defect (Barabas *et al.* 1992a) and linked to crystal water molecules (Debuyst *et al.* 1991), the peaks of the samples D, G and J may

indicate that fluorescence bands are related to the incorporation of water molecules into the crystal lattice or increased internal surface area. The latter hypothesis is consistent with the inferences of Barnes and Taylor (1998) that density and related surface area changes are the main cause of fluorescence.

Figure 2 shows that the signal at g=2.0057 shows severe microwave power saturation effects (compare 2C and 2D). Thus, it is advisable to measure this signal at low microwave powers for quantitative analyses.

We attribute the differences between our results and those of Ikeda *et al.* (1992) to the fact that intensity measurements using a pin hole cavity are critically dependent of the density of the sample. Rather than being an indicator of variation in the concentration of SO_3^-, the intensity of the signal at g=2.0031 recorded the density of the coral slice. The signal at g=2.0007 seems to be related to the fluorescence bands, but the crystallographic aspect has to await further investigation. We conclude that the fluorescence bands of the coral investigated are neither related to SO_3^- (and by implication to SO_3^{2-}) nor to SO_2^-.

	5 kGy				5 kGy, 7 h at 150 °C				
Sample Set	2.0057	2.0031	2.0007	**2.0007**	2.0057	2.0031	2.0007	**2.0057**	**2.0007**
CAB	Y	N	N	N	N	N	N	N	N
FDE	N	N	Y	Y	N	N	Y	N	Y
IGH	Y	N	Y	Y	N	N	N	N	Y
KJL	Y	N	Y	Y	N	N	Y	N	Y

Table 1: Summary of ESR measurements (bold: measurement at 100 mW. Y: ESR signal of fluorescent sample is higher than either of the two surrounding samples; N: it is not higher)

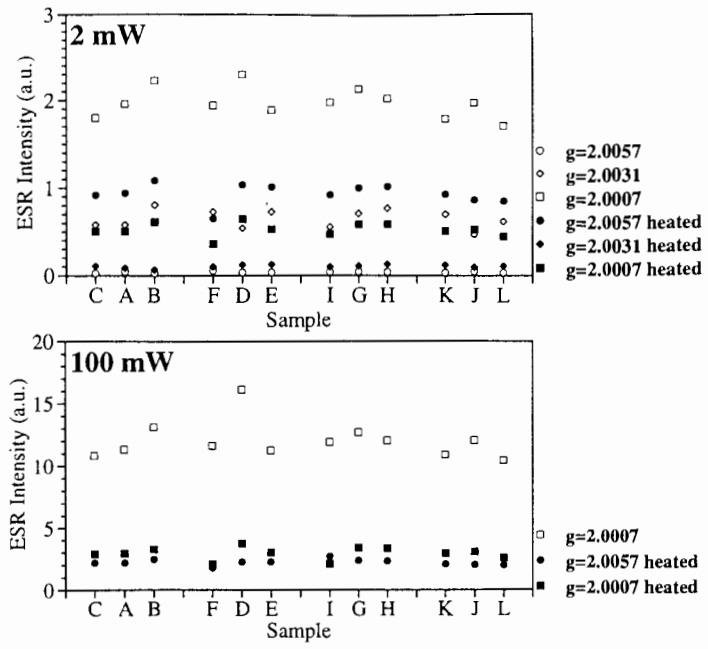

Figure 3.
Intensity measurements of the sample sets shown in Figure 1.Only the signal at g=2.0007 shows a relationship between intensity and fluorescence

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Reviewer

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Comments

The authors have attempted to confirm an earlier study suggesting that fluorescent bands in coral are due to sulfur oxy-anion radicals. Although they observe some weak enhancements in the intensity of some of these signals, they do only see weak enhancements of these signals in the fluorescent bands. However, one of the strongest signal enhancements is seen in the g = 2.0007 peak associated with CO_2^-, which could be strengthened as a result of difference in the texture of the coral (i.e., the packing density or mean size of aragonite crystals in the coral skeleton). This lends support to the idea of that fluorescence occurs preferentially in bands of higher density. It would be desirable to complement any further ESR studies of this problem with complementary, quantitative studies of the fluorescence phenomenon itself, as it is not clear in the present studies whether the material adjacent to fluorescent bands is totally non-fluorescent or is simply less so. As well, more detailed, quantification of coral density would be useful.