AN EPR PALEOTHERMOMETER FOR OIL SHALES

Ney V. Vugman, Henrique A. G. de Moraes and João José F. Sousa
Instituto de Física – Universidade Federal do Rio de Janeiro
P. O. Box 68528 – FAX 55 21 2807693 – Bitnet IFT10010@UFRJ
Rio de Janeiro – Brasil

I. INTRODUCTION

Electron Paramagnetic Resonance spectroscopy (EPR) has been largely used for studying the presence of free radicals in sedimentary organic matter. Unpaired spin concentration of oil shale and coal, with g–values of about 2.0030, is very sensitive to thermal action. Binder (1) reported the change in unpaired spin concentration of coal samples as a function of distance from an igneous intrusion. Ishiwatary et al. (2) reported the change in free radical concentration of recent sediments as a function of laboratory annealing temperature, in the range from 150 to 400 ^{0}C. Sousa et al. (3), using the stratigraphic function of spin concentration, detected an intense thermal influence, produced by diabase intrusion, on the Irati oil shale.

In this paper we report another paramagnetic center measured in oil shale which we call P–center. Isochronous annealing experiments on the Irati oil shale (Paraná Basin – Brasil) stress that the P–center spin concentration is very sensitive to temperature. As an application of this property an EPR thermometer for oil shale is proposed.

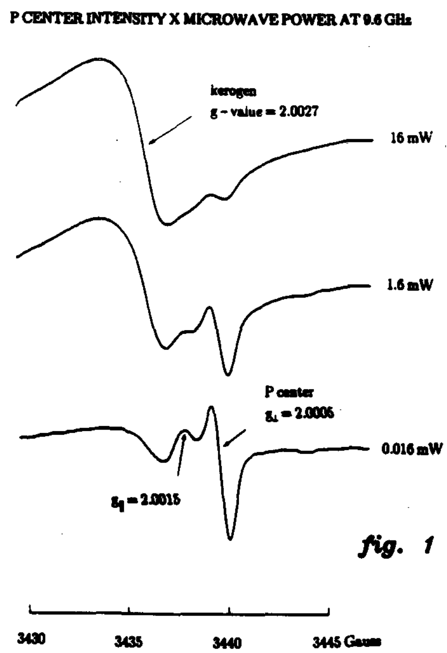


fig. 1

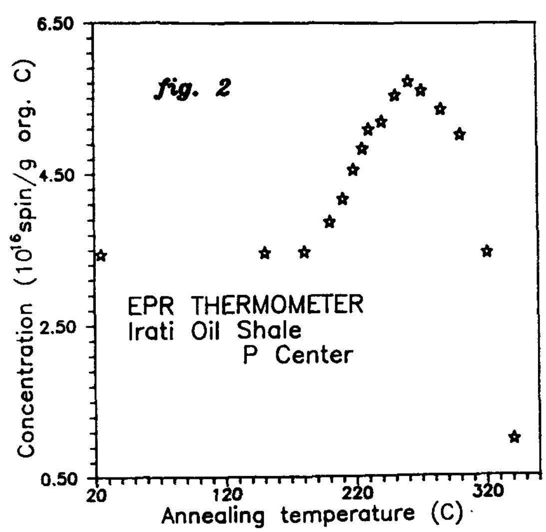


fig. 2

II. RESULTS

P–center cannot be observed at the usual microwave power of oil shale resonance (10^2 mW). Figure 1 shows that 10^{-2} mW is the ideal microwave power for P–center observation. The EPR spectrum corresponds to an axially symmetric powder pattern with a perpendicular g–value = 2.0005 and a parallel g–value = 2.0015.

Isochronous annealing experiments were performed on the Irati oil shale. Sealed samples with 50 mg were heated during 11 hours. The P–center concentration was determined with the aid of a MgO/Cr(III) standardized sample. The dependence of the concentration on the annealing temperature, presented in figure 2, is similar to that exhibited by the oil shale resonance line with $g = 2.0030$, but in that case the temperatures involved are higher. P–center is more sensitive to temperature in the range from 180 to 320 ^{0}C. Maximum concentration is reached around 260 ^{0}C when recombination processes overcome the generation of free radicals.

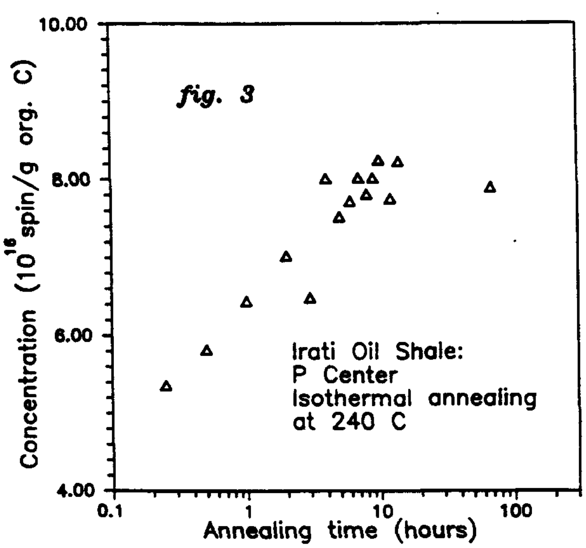
Isothermal annealing experiments were performed at 240 ^{0}C and 330 ^{0}C and are shown in figures 3 and 4. Samples annealed below 260 ^{0}C reach a concentration plateau after about 10 hours. On the other hand, samples annealed above 260 ^{0}C show a fast concentration increase (about 5 min) followed by an exponential decrease (vanishing after 200 hours at 330 ^{0}C).

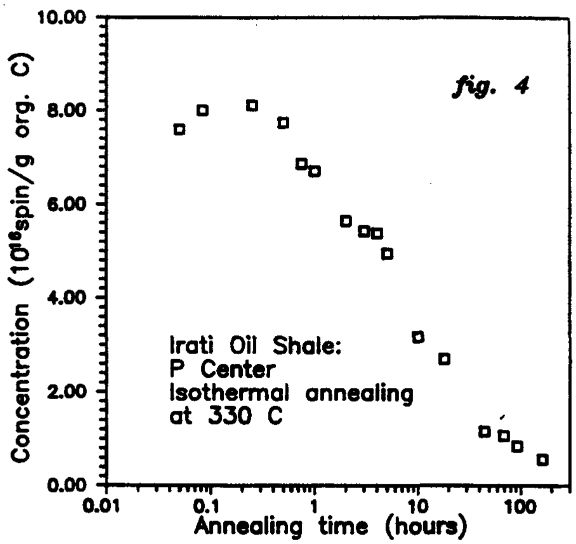
III. THE THERMOMETER

The annealing experiments indicate the possibility of utilizing the P–center as a maximum temperature thermometer for oil shale. The following recipe is proposed:

1) Take an EPR spectrum of your sample (low power) and measure the spin concentration of the P–center (per gram of organic carbon). The use of a well calibrated standard sample is advisable.

2) Compare C_m, the measured concentration, to the thermometer curve shown in figure 2. There will be two possibilities: C_m will correspond to T_{be}, a temperature before the maximum, or it will correspond to some temperature above it.





3) Anneal your sample at a temperature T_{be} + 10 for 12 hours. If the signal increases, T_{be} is the maximum temperature your sample was submitted to (± 10). If the signal does not increase follow step 4.

4) Anneal your sample at 280 ^{0}C for 30 minutes; if the signal does not decrease, gradually increase the annealing temperature until the P signal begins to decrease. This will be the maximum temperature you wish to find out.

5) In this case, it is possible to determine for how long your sample was annealed millions of years ago. Just compare your C_m with a curve similar to that shown in figure 4, but resulting from an experiment run at the maximum temperature you found out earlier.

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REFERENCES

1 – C.R. Binder, Ph.D. Thesis, Pennsylvania State University, 1965, p. 129.
2 – R. Ishiwatary, M. Ishiwatary, B.G. Rohrback and I.R. Kaplan, Geochim. Cosmochim. Acta, 41, 815 (1977).
3 – J.J.F. Sousa, N.V. Vugman and A.S. Mangrich, Chem. Geol., 63, 17 (1987).