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## Identification and valuation of paramagnetic radicals in natural dolomites as an indicator of geological events

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**Abstract** Geological sedimentary dolomite samples from the Superior Proterozoic are studied using electron paramagnetic resonance (EPR) spectroscopy. The complex spectra in the  $g = 2.0$  region is composed of  $Mn^{2+}$  lines and signals due to crystallization and radiation-induced defects. Measurements in microwave frequencies of 9.5 GHz (X-band) and 35 GHz (Q-band), and thermal and/or radiation treatments allowed identification of seven paramagnetic radicals in the  $g = 2.0$  region: (1) isotropic organic radical; (2) axial  $SO_2^-$ ; (3) axial  $PO_2^0$  or  $PO_2^{2-}$ ; (4) isotropic  $CO_2^-$ ; (5) axial  $CO_2^-$ ; (6) axial  $CO_3^{3-}$ ; (7) isotropic unknown line. The use of these paramagnetic centres as indicators of geological events is discussed.

**Keywords** Dolomite · EPR · Gamma radiation · Defects

### Introduction

For 30 years, paramagnetic calcium carbonate minerals have been tested as markers of geological events, such as thermal annealing and crystallization processes, using electron paramagnetic resonance (EPR) (Ikeya 1993). Calcite and aragonite have been the most studied because of their abundance in the Earth's crust. Paramagnetic radicals such as  $CO_2^-$ ,  $CO_3^{3-}$ ,  $CO_3^-$ ,  $SO_2^-$ ,  $SO_3^-$  and  $O^-$  with orthorhombic, axial and isotropic symmetry were identified in these minerals when submitted to ionizing radiation (Marshall et al. 1968; Serway and Marshall 1967; Callens et al. 1994; Katzenberger et al. 1989; Kai and Miki 1992; Schramm and Rossi 1996).

Some of these radicals such as  $CO_2^-$ ,  $CO_3^{3-}$ ,  $SO_3^-$ , have a long mean life, which permits their use in dosimetry and geochronology (Henning 1983; Ikeda et al. 1992; Molodkov 1993).

In dolomites,  $CaMg(CO_3)_2$ , the  $Mn^{2+}$  ion is a natural substitutional impurity at the sites of both  $Ca^{2+}$  and  $Mg^{2+}$  ions. The occupation ratio (K) of the  $Mn^{2+}$  ions at these sites ( $K = Mn^{2+}$  at  $Mg^{2+}$  site/ $Mn^{2+}$  at  $Ca^{2+}$  site), determinable from the EPR spectra, has been investigated by several authors and related to dolomite origin (Wildeman 1970; Kretz 1982; Lumsden and Lloyd 1984; Lloyd et al. 1993). However, few studies have been done which could identify paramagnetic defects in dolomites. Lloyd and Lumsden (1987), in particular, considered that the intensity of the line at  $g = 2.0023$  could be correlated with thermal treatment suffered by the mineral and consequently be used as a paleothermometer. However, no complete interpretation of the EPR spectra of dolomites in the region  $g = 2$  is as yet accepted.

In this work, we studied the EPR spectra of geological dolomites from sedimentary origins. Measurements at microwave frequencies of 9.5 GHz (X-band) and 35 GHz (Q-band) in natural, heated, and reirradiated samples permitted identification of some of the paramagnetic species present in the EPR spectra in the  $g = 2.0$  region.

### Experimental

We examined four sedimentary dolomites from Goiás, Brazil, dated from the Superior Proterozoic (500–900 ma), which had been subjected to low metamorphism (350–500 °C, 3–5 kbar). Chemical analysis using atomic absorption spectroscopy showed the  $Mn^{2+}$  ion concentration ranging from 15 to 150 ppm. Powdered samples with grain sizes ranging from 80 to 125  $\mu m$  were prepared in an agate mortar with and without twist, which were separated.

One hundred-mg aliquots of the samples were subjected to thermal treatments at temperatures ranging from 150 to 600 °C, for 24 h, in both ambient and argon (Ar) atmospheres. Natural and heated samples were subjected to a maximum radiation dose of 4 kGy using a  $^{137}Cs$  source radiating 40 Gy  $min^{-1}$  ( $\pm 4\%$ ).

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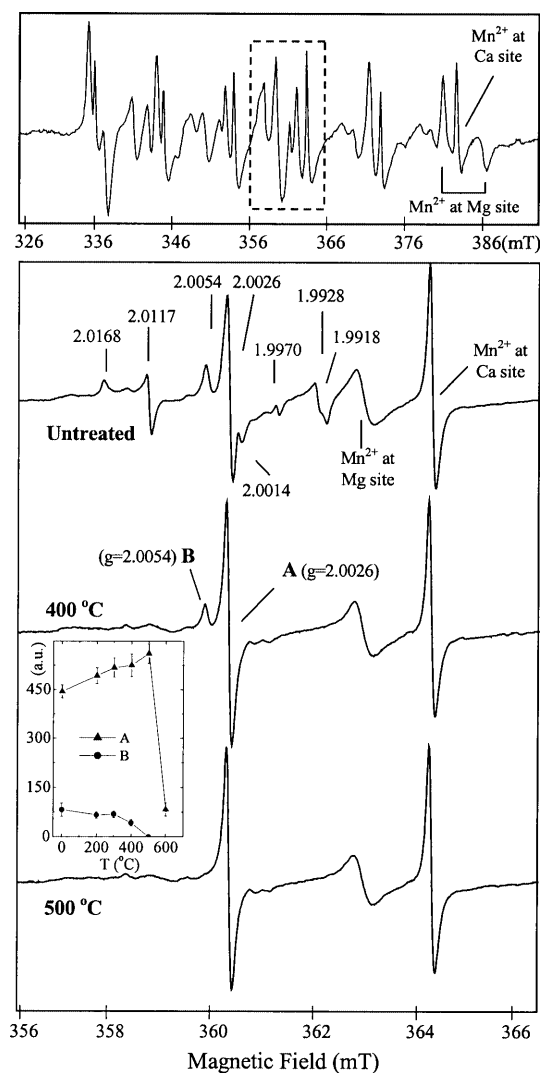
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The dolomites were analyzed at room temperature by EPR spectroscopy using a Bruker ESP 300E spectrometer, operating at 9.5 GHz (X-band) and 35 GHz (Q-band). The  $g$  factors were referenced by a pitch signal ( $g = 2.0028$ ).

## Results and discussion

The preparation with and without twist of the samples did not affect the type and intensity of the radicals, because the equal spectra were obtained for two preparations of all samples. We adopted the standardized preparation without twist. An identical spectrum was also obtained of a rock piece.

In Fig. 1 at the top is shown the complete sextet of the  $Mn^{2+}$  spectrum of the dolomite, identifying the



**Fig. 1** X-band EPR spectrum of untreated 17A rock with the  $Mn^{2+}$  sextet indicating by dashed line the region of interest (top), and zoom spectra of the untreated sample, and samples submitted to thermal treatments at 400 and 500 °C. The inset shows the behavior of the lines A and B with thermal treatment. All spectra were obtained at room temperature

central region of interest from 356 to 366 mT. In the last line of the sextet (high field) the lines associated with occupation of  $Mn^{2+}$  at the Ca site and the Mg site in the dolomite are indicated. In addition to the  $Mn^{2+}$  spectrum, EPR spectra of all studied samples showed essentially the same lines in the  $g = 2$  region with variable relative intensities (Fig. 1). The inset in Fig. 1 demonstrates the behavior of the radicals A and B with thermal treatment. Thermal treatments at 400 °C for 24 h destroyed most of the lines (Fig. 1b,c), leaving only those at  $g = 2.0054$  and  $g = 2.0026$ , which increased with temperatures up to 500 °C. The line at  $g = 2.0026$  was the only one left when 500 °C was reached, and it decreased at 600 °C. This line can therefore be attributed to an isotropic species (radical A). The line at  $g = 2.0054$  is attributable to another species (radical B).

A sextet and doublets of forbidden transitions between the sextet lines characterize the  $Mn^{2+}$  spectra. Comparing the Fig. 1 spectra with others of our dolomite samples, we verified that the doublet of forbidden transitions is hidden between the line at  $g = 2.0168$  and that at  $g = 1.9970$ . However, this doublet is of low intensity with respect to the other lines in this spectrum region. This can be observed in the spectra of the dolomites heated at 400 and 500 °C, which shows that the  $Mn^{2+}$  lines at 362–364 mT were unaltered with thermal treatment. Furthermore, significant intensity of the forbidden transitions with respect to radicals A and B was not observed.

The increase of radical A with temperature suggests that it could be related to organic radicals produced by, for example, decomposition of the humic acids usually present in dolomites.

Radical A does not form when pure inorganic calcium carbonate samples are irradiated. As a consequence, it could not be associated with an inorganic carbonate-type radical. Moreover, the dolomite rocks studied in this work originate in sediment. In this case, organic matter is generally incorporated as a minor component. Therefore, the  $g = 2.0026$  species could originate in this decomposed organic matter. In our samples an organic matter concentration ranging from 0.15 to 0.40% was detected.

Paramagnetic radicals produced from organic matter decomposition can show stability at temperatures up to 500 °C. One example is the isotropic ( $g = 2.00275$ – $2.00290$ ) species associated with kerogen from oil shale of a stratigraphic column of the Irati (Paraná Basin, Brazil) formation studied by Sousa et al. (1987). The authors showed that radical concentration, which is related to the EPR signal intensity, increases as the temperature of samples increases to 500 °C. A similar behavior was also observed for the variation of the EPR signal intensity as a function of the stratigraphic column depth. Considering that higher temperatures are associated with great burial depths, the authors suggested that the kerogen EPR signal could be used to trace the relative temperature levels to which sediment has been submitted.

The lines at  $g = 2.0168$ ,  $g = 2.0117$ ,  $g = 1.9928$ , and  $g = 1.9918$  showed the same behavior when heated and irradiated. These lines could be linked to the paramagnetic species C, which has axial symmetry and hyperfine structure due to the interaction of the unpaired electron with an  $I = 1/2$  nuclear spin. Simulation of the experimental spectrum using Bruker Symphony software (Fig. 2) confirmed this hypothesis and showed that this spectrum is associated with an axial center having  $g_{\perp} = 2.0023$  and  $g_{\parallel} = 2.0043$ , and hyperfine coupling constants of  $A_{\perp} = 4.30$  mT and  $A_{\parallel} = 3.26$  mT. This species C is probably related to a phosphate radical (phosphorous has  $I = 1/2$  nuclear spin). In all samples studied,  $P_2O_5$  was detected by chemical analysis. Moreover, it is known to be sometimes present as a substitutional impurity in dolomite and calcite structure, resulting in  $PO_2^{\cdot-}$ ,  $PO_2^{\cdot0}$ , and  $PO_2^{\cdot3-}$  radicals (Atkins and Symons 1967, Marfunin 1979). However,  $PO_2^{\cdot3-}$  generally has a large hyperfine structure (45–70 mT) and is thus not related to the radical detected in our dolomites. Therefore, the phosphate radical can be attributed to either a  $PO_2^{\cdot2-}$  or  $PO_2^{\cdot0}$  radical.

Spectra taken at the Q-band frequency show that line B at  $g = 2.0054$  is the result of line superposition of  $g_{\perp} = 2.0048$  and  $g_{\parallel} = 2.0054$  of an axial species (Fig. 3). Species B may therefore be attributed to the same  $SO_2^{\cdot-}$  radicals produced by radiation in calcite (Kai and Miki 1992). The Q-band measurements in heated (150 °C) and reirradiated samples also allowed identification of species D ( $g_1 = 2.0033$ ,  $g_2 = 2.0014$ , and  $g_3 = 1.997$ ) and E ( $g = 2.0007$ ), which have  $g$  values similar to those of orthorhombic and isotropic  $CO_2^{\cdot-}$ , respectively (Atkins and Symons 1967; Marshall et al. 1968; Marfunin 1979; Rossi and Poupeau 1989). These radiation defects are usually observed in irradiated calcite and aragonite and used as dose markers for these minerals. Species E is not formed in samples heated at temperatures higher than 200 °C, confirming its attribution to  $CO_2^{\cdot-}$  radicals connected to water molecules in motion (Atkins and Symons 1967; Marfunin 1979; Rossi and Poupeau 1989).

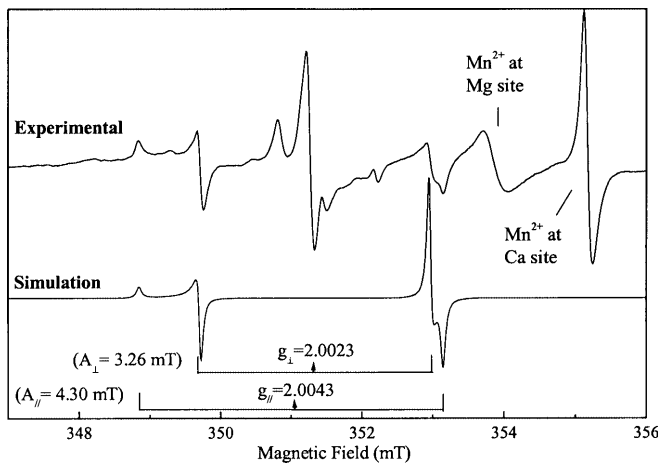


Fig. 2 X-band spectrum of untreated rock 17A (a) and simulation of species C (b) with  $g$  and  $A$  axial symmetry

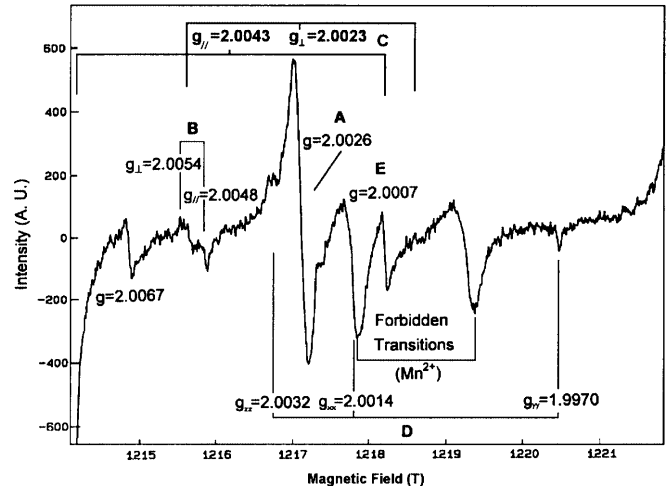
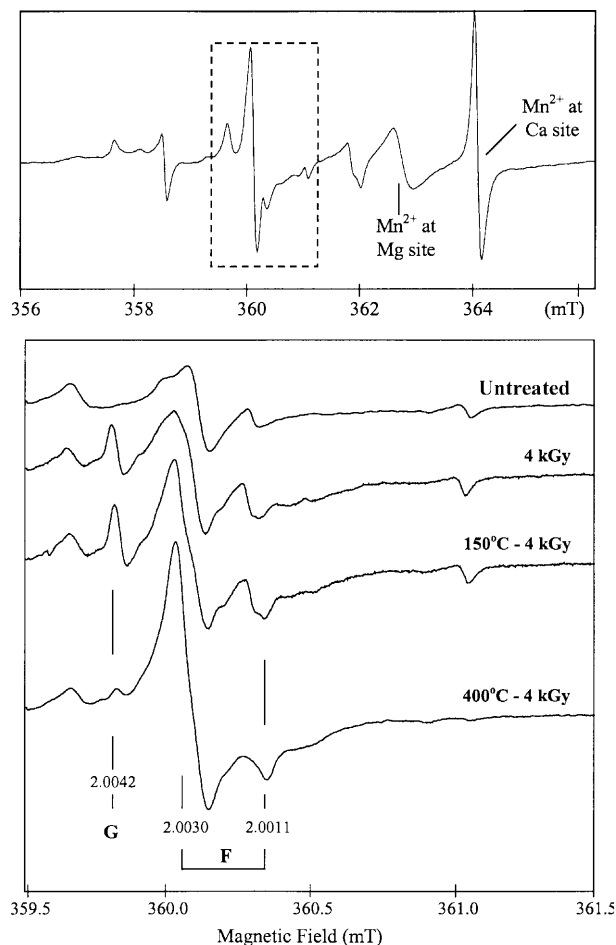


Fig. 3 Q-band spectrum of untreated rock 17A indicating A, B, C, D, and E paramagnetic species

Measures taken of heated (150 and 400 °C) and re-irradiated samples, and presented in Fig. 4, indicate that lines at  $g = 2.0030$ ,  $g = 2.0011$ , and  $g = 2.0042$  are related to a species with axial (F,  $g_{\perp} = 2.0030$  and  $g_{\parallel} = 2.0011$ ) and isotropic (G,  $g = 2.0042$ ) symmetry, respectively. Species F has  $g$  values similar to those of the radical  $CO_3^{\cdot3-}$  with axial symmetry (Chantry et al. 1962; Serway and Marshall 1967; Marshall et al. 1968; Marfunin 1979; Rossi et al. 1985). This radical was also detected in our other irradiated dolomites, whether subjected to medium metamorphism (500–600 °C, 2–6 kbar) or not. Species G was not identified, but has also been detected by other authors (Chantry et al. 1962; Serway and Marshall 1967).

The heat treatment decreased the EPR signal intensity at higher temperatures in the treatments carried out in the Ar atmosphere. This suggests that the presence of oxygen causes recombination in this paramagnetic species. Isothermal annealing experiences showed that the intensity of radical A decreased with heating at 600 °C, at which temperature the dolomite structure decomposes (Goldsmith 1980). Species B, C, D, and E are stable at up to 400, 300, 250, and 150 °C, respectively. Species G presents a mean life of 10 min as shown in the isothermal annealing experiment at 100 °C. Thermal behavior of species F as indicated by EPR was not verified in detail because it is superimposed on lines belonging to species A and D. However, it can be shown that the intensity of these sets of lines (F + A + D lines) decays and stabilizes after 15 minutes of heating at 100 °C. Similar behavior was observed by Lloyd and Lumsden (1987) for the same signal ( $g \approx 2.0023$ ) in geological dolomite samples. These authors maintain that there is an intensity reduction of this signal with the temperature increase as with geological events, which would justify the use of this line as a paleothermometer. In fact, however, as the  $g \approx 2.0023$  line is a composite signal, its decay results from the decay of lines belonging to species D ( $g = 2.0032$ ), F ( $g_{\parallel} = 2.0030$ ), and A ( $g = 2.0026$ ).



**Fig. 4** Spectra of rock 17A untreated indicating by *dashed line* the region of interest (*top*), and zoom spectra of the untreated and irradiated with 4-kGy samples. The last two spectra correspond to samples previously heated at 150 and 400 °C, and irradiated. All spectra were obtained at room temperature

As the intensity of line A increases at heating temperatures up to 500 °C, we can conclude that lines D and F are responsible for the decay of the signal at  $g \approx 2.0023$ . From our point of view, the use of the line at  $g = 2.0023$  as a paleothermometer, as suggested by Lloyd and Lumsden, does not have to be considered because these lines are sensitive to both radiation and temperature.

The EPR spectra of heated (150 and 400 °C) and reirradiated samples show that radical A is not sensitive to gamma radiation. Species B, C, and D present little sensitivity to radiation doses, while species F is highly affected by radiation. The good stability of radicals B, C, D, and E with respect to a temperature range of 150–400 °C suggests that they could be appropriate for dating geological events.

## Conclusion

This study has shown that the complex EPR spectra of sedimentary dolomites in region  $g = 2$  are attributable

**Table 1** Paramagnetic radicals detected in the dolomites studied

Species	g factors/A (mT)	Probable attribution
A	$g = 2.0026$	Organic radical
B	$g_{\perp} = 2.0054, g_{\parallel} = 2.0048$	$\text{SO}_2^-$
C	$g_{\perp} = 2.0023, g_{\parallel} = 2.0043$ $A_{\perp} = 3.26, A_{\parallel} = 4.30$	$\text{PO}_2^0$ or $\text{PO}_2^{2-}$
D	$g_1 = 2.0014, g_2 = 1.9970,$ $g_3 = 2.0032$	$\text{CO}_2^-$
E	$g = 2.0007$	$\text{CO}_2^-$
F	$g_{\perp} = 2.0030, g_{\parallel} = 2.0011$	$\text{CO}_3^{3-}$
G	$g = 2.0042$	–

to at least seven paramagnetic radicals in addition to  $\text{Mn}^{2+}$  (Table 1). Most of them are produced by radiation and also have been identified in irradiated calcite and aragonite. In the  $g = 2.0023$  region, the spectra are composed by superposition of three paramagnetic species. Orthorhombic  $\text{CO}_2^-$ , which is not observed in the spectrum of carbonate-containing Mg, is produced, however, in dolomites. Dose indicator centers of calcite and aragonite samples, such as isotropic  $\text{CO}_2^-$  radicals, are also present in the EPR spectra of the studied dolomites, suggesting that this mineral could be used for dosimetric purposes. Consequently, additional work must be done to estimate the dolomite potential of EPR for dating and dosimetry.

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