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Potential of EPR imaging to detect traces of primitive life in sedimentary rocks

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ABSTRACT

In the prospect of the search for traces of primitive life on Earth and Mars, we investigated the possibility to detect and visualize the spatial distribution of minute amounts of organic matter in ancient rocks, in a non-destructive way, by Electron Paramagnetic Resonance Imaging (EPRI). We studied a series of non- or moderately metamorphosed siliceous rocks (cherts) of different ages ranging from 45 Ma to 3490 Ma and embedding fossile organic matter. In the case of the oldest cherts containing only mature insoluble organic matter (IOM), with $IOM^{\bullet}$ radicals characterized by a single Electron Paramagnetic Resonance (EPR) line, we could obtain three-dimensional images with sub-millimetric resolution of the organic matter distribution inside samples containing as low as 10^{14}–10^{15} radicals per gram. In the case of younger cherts, containing less mature organic matter, and thus several types of organic radicals, we showed that selective imaging of each type of radical was possible provided that the EPR spectra did not overlap. Selective imaging of either the organic radicals or of the oxygen vacancy (E' centres) of the mineral matrix, which are ubiquitous in siliceous rocks, was possible, selecting either one or the other paramagnetic species with high power in-phase, 1st harmonic detection or with 90°-out-of-phase, 2nd harmonic detection of the EPR. The influence of ferromagnetic inclusions in the mineral matrix on the EPRI of the organic matter was also addressed. Image artifacts due to the ferromagnetic resonance signal of these inclusions could be easily removed by background substraction from the EPR spectra before image reconstruction. We thus showed that selective imaging by EPR of minute amounts of fossile organic matter in ancient rocks could be possible despite the magnetic complexity of such materials.

1. Introduction

Traces of ancient life on Earth and possibly on Mars should occur as minute amounts of fossil carbonaceous material embedded in rocks. This carbonaceous material should be essentially an insoluble organic matter (IOM), made of a polyaromatic macromolecular material, which is solvent insoluble and acid resistant and therefore very difficult to analyse (Tissot and Welte, 1978). Therefore, detecting and determining the origin of this carbonaceous matter, whether terrestrial or martian, is highly challenging from the point of view of sample analysis. However, along with the determination of its detailed chemical structure, the visualization of the distribution of the IOM within ancient terrestrial or martian rocks is of primary importance and may provide valuable data when tracing back the history and the origin of this IOM.

In the particular case of such natural samples, a suitable imaging technique should comply to several specific constraints. It should be: (i) sensitive enough to map out the distribution of a few tens of micrograms of IOM in millimeter to centimeter size samples, (ii) non destructive and quarantine adapted in the specific case of martian samples, (iii) harmless to the fragile IOM. Optical, Raman or electron microscopies are frequently used to visualize and analyze the organic matter within rocks (Kudryavtsev et al., 2001; Schelbe et al., 2004; De Gregorio and Sharp, 2006; Schopf et al., 2007) since they combine high spatial resolution (down to the micrometer or nanometer scale) with good sensitivity. However they are all limited to surface imaging or require tedious and destructive thin slice cutting if bulk imaging is desired. Besides, in the case of Raman and electron microscopies, chemical and structural changes may be induced in the IOM upon analysis due to the high energy laser or electron beams employed. Therefore imaging techniques using probing radiation with low energy and penetrating a whole centimeter size sample are to be preferred. Techniques based on nuclear or electron magnetic resonance are thus more likely to fulfil the above requirements. These techniques do not require any sample preparation. Besides, they are based on weak magnetic dipole transition, so that a full penetration of the micro- or radiowaves into the sample with weak energy deposition is ensured. Due to the low abundance of IOM in very old rocks, which may be as low as a few tens of ppm (Beaumont and Robert, 1999), imaging of the IOM based on nuclear magnetic resonance is not possible. On the opposite, Electron Paramagnetic Resonance Imaging (EPRI) is likely to be perfectly adapted to such materials. We showed in previous works (Gourier et al., 2004;

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Skrzypczak-Bonduelle et al., 2008) that, even in the oldest rocks aged of 3.5 Ga, the IOM contains up to 10^{16}–10^{17} radicals per gram, which can be easily detected by Electron Paramagnetic Resonance (EPR). We showed that the EPR signature of the radicals in the IOM was very sensitive to changes in the chemical composition and in the dimensionality of the radical distribution at the microscopic scale, so that the radicals could be used as tracers of the maturation state of the IOM, and as age markers of the IOM in non or weakly metamorphosed cherts (Skrzypczak-Bonduelle et al., 2008). Also, in the case of IOM from carbonaceous meteorites, the EPR signal exhibits characteristics that are different from terrestrial IOM (Binet et al., 2002, 2004a,b; Gourier et al., 2008).

The aim of the paper is to assess the potential of EPRI to visualize the distribution of paramagnetic species, including radicals in the IOM, within ancient siliceous rocks. The relevance of EPRI has to be examined regarding the chemical and magnetic complexity of such materials. As a matter of fact, ancient siliceous rocks may contain several types of magnetic species, either in the organic material or in the mineral matrix. Terrestrial fossil organic materials may exhibit more or less complex EPR signatures, depending on their maturity stage. Organic materials in non-metamorphosed Phanerozic rocks generally contain a miscellany of radicals altogether, either isolated molecular radicals or radicals linked to the IOM fraction, hereafter referred to as $IOM^{\bullet}$ radicals (Griffiths et al., 1982; Gourier et al., 2004; Skrzypczak-Bonduelle et al., 2008), so that the EPR signature of Phanerozoic organic materials is complex and made of several overlapping signals. On the opposite, more mature organic materials as found in non- or moderately metamorphosed Precambrian rocks, contain only $IOM^{\bullet}$ radicals so that their EPR signature is very simple, made of a single EPR line (Gourier et al., 2004; Skrzypczak-Bonduelle et al., 2008). However, it is important to note that the shape of the EPR line of Precambrian IOM is very similar to that of meteoritic IOM (Binet et al., 2002). Regarding Martian organic matter, if ever detectable, it is impossible to figure out at present what its EPR signature should look like. Depending on its origin, extraplanetary, chemical or possibly biological, and on its specific evolution under martian conditions, EPR signatures similar to those of Phanerozoic or Precambrian terrestrial matters can be both expected. The mineral host may also contain several magnetic species. Siliceous rocks generally contain different intrinsic defects including oxygen vacancies known as E' centres (Weil, 1984). Inclusions of ferromagnetic minerals may also occur. The latter are highly expected in the case of martian samples owing to the significant abundance of iron oxides at the surface of Mars (Chevrier and Mathé, 2007). The simultaneous occurrence of several signals in the EPR spectrum of a sample may prevent the discrimination between paramagnetic species by EPRI. Therefore, the possibility of selective imaging of each type of paramagnetic species in the case of ancient siliceous rocks has to be addressed. Ferromagnetic inclusions in the samples generate large and intense ferromagnetic resonance signals manifesting themselves as a background distortion in the smaller spectral range of the EPR signals from the organic material. Therefore, the influence of ferromagnetic resonance signals on the imaging of the IOM by EPR has to be examined. To demonstrate the feasibility of EPRI with ancient siliceous rocks, we studied by EPRI a series of cherts (microcrystalline quartz) of different ages ranging from 45 Ma to 3490 Ma and containing fossil IOM. The selected samples exemplify the different cases above mentioned.

2. Experimental part

All the chert samples were provided by *Museum National d'Histoire Naturelle* (Paris, France). The oldest sample, of Archean age and referenced as PPRG 006 from Precambrian Palebiology Research Group (courtesy of W. Schopf) is a bedded sedimentary chert from the Dresser Formation (3490 Ma), Warrawoona Group, Pilbara craton in Australia. It was collected in the lower chert horizon of the so-called Towers Formation [and since 1983 reassigned to the Dresser Formation (Van Kranendonk, 2006)], in the North Pole B Deposit Mine from the upper lip of the open cut on the west side; Marble Bar 1:250,000 map sheet grid ref number 223357. The metamorphic grade is within the prehnite–pumpellyite to lowermost greenschist facies (Buick et al., 1981; Awramik et al., 1983). Recent investigation of the chemical structure of the kerogen in this chert revealed the existence of aliphatic carbon atoms along with relatively large aromatic units, with however no graphitic character, indicating that the kerogen did not experience any severe thermally induced chemical modification (Derenne et al., 2008). Cherts from the Dresser Formation are reported to host the oldest but controversial stromatolites and microfossils (Dunlop et al., 1978; Awramik et al., 1983; Schopf, 1992; Buick, 1990; Lowe, 1994; Schopf, 2004). Nevertheless, the carbon isotope composition (Strauss and Moore, 1992; Beaumont and Robert, 1999) and an odd-over-even carbon number predominance in aliphatic chains (Derenne et al., 2008) point to a possible biological origin of the kerogen. One sample of Paleoproterozoic age, referenced as GF 74-1-11 from Awramik collection comes from the Schreiber Beach locality of the Gunflint Formation (1880 Ma) in Ontario (Canada). This non-metamorphozed chert is known to contain uncontested prokaryotic microorganisms (Barghoorn and Tyler, 1965). Another chert (not referenced) of Lower Devonian age from the Rhynie Formation, Scotland (396 Ma) is the earliest known siliceous hot spring deposit from a continental geyser activity (Rice et al., 1995). It is well known for preserving with remarkable details an early Devonian freshwater and terrestrial community of animals and plants, bacteria and fungi. The youngest chert sample, referenced as PPRG 456 from Schopf collection comes from the Clarno Formation, John Day basin, in Oregon, USA (Eocene, 45 Ma). This chert contains well preserved fossils of vascular plants.

Before EPR analysis, one sample of the Clarno chert and another one of the Rhynie chert were submitted to a series of successive thermal treatments under vacuum, each during 15 min and separated by steps of 50 °C. The final temperature was selected so as to enhance the EPR signals of either the radicals in the insoluble organic matter ($IOM^{\bullet}$ radicals) in the case of the Rhynie chert or both the $IOM^{\bullet}$ radicals and the $CH_3^{\bullet}$ radicals in the case of the Clarno chert. The characteristics of the samples and the treatments preliminary to EPR analysis are summarized in Table 1. Before EPRI experiments, the

Table 1
Sample characteristics

Geological setting/country	Age	Macroscopic features	Sample size (mm × mm × mm)	Thermal treatments	Peak-to-peak linewidth of the EPR signals (mT)	Radical concentration (g^{-1})
Clarno Formation/USA	45 Ma	Uniformly dark	12 × 3.8 × 3.7	Cumulative treatments up to 300 °C	$IOM^{\bullet}$: 0.54 $CH3^{\bullet}$: 0.1	$IOM^{\bullet}$: 2.5×10^{16} $CH3^{\bullet}$: 2.0×10^{14}
Rhynie Formation/Scotland	396 Ma	Presence of millimeter sized fossils	1.2 × 4.1 × 14	Cumulative treatments up to 495 °C	$IOM^{\bullet}$: 0.60	3.8×10^{15}
Gunflint Formation/Canada	1880 Ma	Uniformly dark	3 × 3 × 11	none	$IOM^{\bullet}$: 0.41	1.5×10^{16}
Dresser Formation, Warrawoona Group/Australia	3490 Ma	Uniformly dark	2.6 × 3.1 × 12.5	none	$IOM^{\bullet}$: 0.16	1.1×10^{15}