Mineralogical applications of EPR spectroscopy

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1. Introduction

. EPR is useful to identify the sorption mechnisms at mineral/liquid literface by using suitable paramagnetic species as a spin probe. Also, EPR is powerful useful to see the effect of alpha-radiation of natural actinide elements (U, Th) to certain minerals over geological time scale. This is based on the ESR detection of paramagnetic defect produced by natural alpha radiation[1]. Here we presents EPR applications to the study ESR spectroscopy has been widely used for fundamental research in many fields, and extended to mineralogy[2]. The sorption and migration of radionuclides in the geosphere is of interests in the geological disposal of radioactive waste. We have applied EPR spectroscopy to monitor the processes related to those phenomena sorption mechanism and migration in mineral environments.

2.Experimental

Sorption mechanism of transition metal ions at mineral/liquid interface has been studied by using Cu(II) as a spin probe. And the migration of actinides has been studied around the uranium ore deposit (Koongaarra) which is located in the Northern Territory of Australia. This orebody has been studied as an natural analogue for the migration behavior of actinides in radioactive waste.

ESR Measurement: All ESR measurement were made at X-band (9.6 GHz) and room temperature on a Bruker EMX spectrometer.

3.Results & Discussion

EPR spectroscopy can identify the sorbed state of paramagnetic ions at mineral/water interface. Figure 1 present the *in situ* measurement of Cu(II) ion sorption at mineral surface with varying solution pH conditions. The change in spectral pattern is due to the changing sorption mechanism with varying pH conditions. The isotropic peak which is due to the free tumbling molecular motion of weakly sorbed ion-exchanged species loses its intensity with increasing pH conditions where strongly sorbed species is dominant by forming inner sphere surface complexes with mineral surface(Figure 1). By closely analyzing the EPR spectra, one can determine the sorption mechanisms and structural information on mineral-metal surface complexes[3].

Figures 2,3 show the typical ESR spectra of some natural samples around Koongarra uranium orebody. In general, samples exhibit a characteristic ESR spectra consisting of two main group of resonances: (I) a group of lines at low magnetic field values, centered at $g\sim4.2$ and (II) lines at higher field values, centered at g~2.0. This resonance line(II) is attributed to lattice defect center produced by alpha-radiation. The intensity of absorption peak in g~2.0 region is closely related to defect center concentration. The resonance lines(I) are attributed to be arising from Fe3+ ion impurity in the mineral lattice . We need to pay attention to the absorption lines at g~2.0 which arises from defect center in the samples. Figure 2,3 show ESR spectra of W1 and AD1 boreholes samples, respectively, with varying depths. The intensity of defect center peak at g~2.0 is very strong in all W1 samples. However, ESR spectra from AD1 borehole samples exhibited relatively weak compared to those of W1. W1 borehole is located inside of the primary uranium orebody zone. AD1 borehole is located near the orebody. This means W1 borehole samples experienced much alpha irradiation from actinide elements in the orebody than those of AD1 samples. The samples far away from the orebody exhibited virtually no defect center peaks. These results imply that the concentration of defect center is a measure of alpha radiation dose over long time scale. In general, a good correlation was achieved between defect center concentration and actinide elements(U, Th).

4.Conclusions

- The sorption mechanism of some paramagnetic species on mineral surface can best be determined by using EPR spectroscopy.
- It was found that some clay minerals are keeping the record of past migration history of actinides within the defect center.
- ESR spectroscopy was useful to quantify defect center produced by natural alpha irradiation.
- ESR method may provide a unique tool for studying past history of actinide migration in the geosphere over geological time scale.

References

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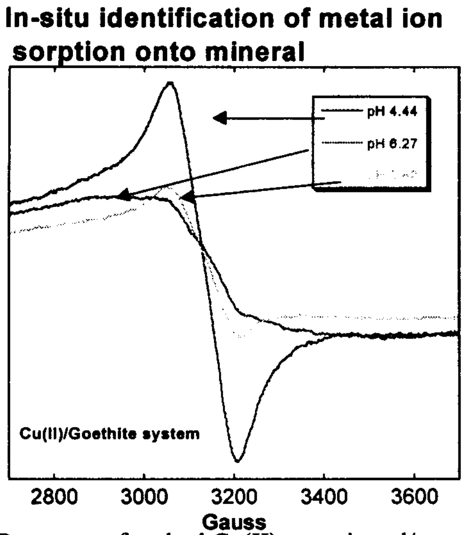

Figure 1. EPR spectra of sorbed Cu(II) on mineral/water interface

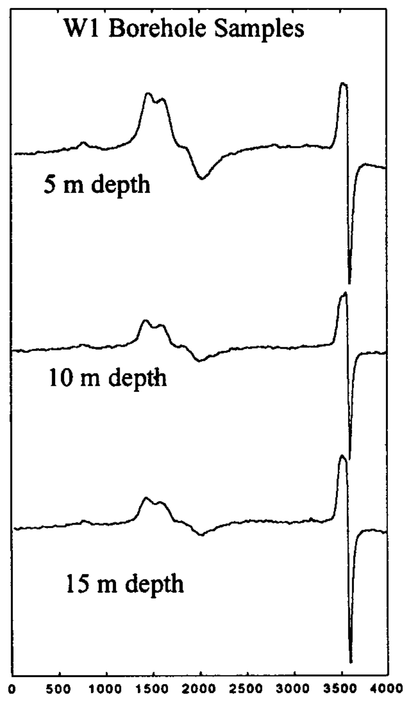

Figure 2. EPR spectra of W1 borehole samples

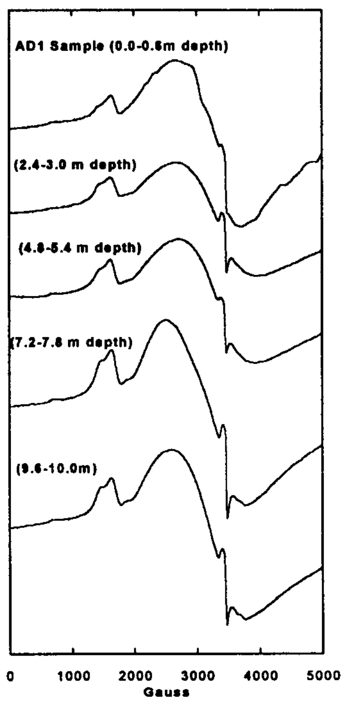

Figure 3. EPR spectra ofAD1 borehole samples