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Iron bearing materials which are found together with different kinds of uranium ores were identified as maghemite or hematite and a chlorite-like material using Mössbauer spectroscopy.

The present work was pursued in an attempt to help to understand the genesis of some type of uranium deposits on sandstones.

Field observations have shown that highest concentrations of uranium ores /pitchblende/ on sandstones are accompanied by strong reddish, brownish and violet pigmentation due to iron oxides or hydroxides[1]. The study of those ores has shown that most of them were originally associated with simple mineralogical conformations and that the complexity was introduced on later stages of development[2]. Therefore it is of geochemical interest to study the development of the uranium minerals from the original uranium bearing solutions. Besides, any compound present in the system, which may undergo transformations related

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to those in the uranium compounds, may act as a probe to follow the main processes.

The main primary uranium bearing minerals are uraninite, a well crystallized UO_2, and the microcrystalline pitchblende. With increased oxygen concentration schoepite coexists as well[3]. Oxidation may convert them into soluble compounds which can be transported by means of ground-waters to the reduction zones where they precipitate and exhibit a great stability. Phase diagrams show that pure water is a poor transport agent for uranium. But this situation is improved if CO_2 is in the medium, due to the formation of several complex ions, $\left[UO_2/CO_3/_3\right]^{-4}$ and $\left[UO_2/CO_3/_2/H_2O/_2\right]^{-2}$, among others[4,5]. These complexes after being precipitated suffer a decomposition and dehydratation, and may reappear as pitchblende. It seems suitable to follow another of the parallel processes which may occur,

$$Fe^{2+} + 2\ HCO_3^- \rightleftharpoons Fe/HCO_3/_2$$

which introduces a Mössbauer active element /^{57}Fe/.

If oxygen is present in the solution the bicarbonate decomposes following the reaction:

$$2Fe/HCO_3/_2 + 1/2\ O_2 \rightleftharpoons Fe_2O_3.H_2O + 4CO_2 + H_2O$$

The $Fe_2O_3.H_2O$ precipitation and simultaneous CO_2 liberation /which remains in solution/ are deeply related to the pigmentation of the ores, as will be seen below. Besides, it is enough a small change in the environment to pass from Fe^{2+} to Fe^{3+} and viceversa. Besides oxidation of Fe^{2+} is more complete in

alkaline solutions, situation which corresponds to ground waters.

It has been shown experimentally that iron bearing solutions at rest and in contact with air[6] form simultaneously red and ochre oxides. The red ones are produced as a film on the surface and the ochre ones in the bulk of the solution. These compounds have been identified by X-ray work as γ -$Fe_2O_3.H_2O$ /lepidocrocite/ and α-$Fe_2O_3.H_2O$ /goethite/ being both compounds ochre, but lepidocrocite is unstable, being converted to γ-Fe_2O_3 /maghemite/ which is red. This compound is metastable and may pass to α-Fe_2O_3 /hematite/ which is red as well[6,7]. The γ-form of the hydrated oxide is present generally on the surface because the concentration of CO_2 is lower here than in the bottom where, in general, the α-form which requires higher CO_2 concentrations, is present.

Two samples from the Sierra Pintada uranium district /Mèndoza, Argentina/ were studied. The first sample was taken from the red bands of the host rock and the other one from the yellow bands /lower level/. They were isolated through manual picking up of the quarz particles /0.1 - 0.4 mm/ on which they were deposited as a very thin film. They were representative of two kinds of uranium containing sandstones: one /red/ with much higher uranium content than the other. Further separation of the coloured material was not possible. X-ray diagrams were made but the identification was unseccesful as the quarz lines mask the diagram. At this stage the Mössbauer spectroscopy seemed appropriate to give some information[8-11].

Samples were encapsulated between acrilic discs. An Elron Mössbauer spectrometer in the constant acceleration mode was used together with a 10 mC ^{57}Co source in a copper matrix and an Ar/CO_2 filled Reuter Stokes RSG 61 proportional counter. The runs were made at room temperature and the counts per channel /N/ had a statistical error of approximately one tenth of the intensity of the weakest peak. In the case of the red sample, N was of the order of 6×10^5 counts/channel and therefore $N^{1/2}$, the statistical error, 7.8×10^2 and the percentage statistical error, 0.13 % whereas the weakest peak is 1.5%.

The ochre sample /Fig.1/ shows three peaks in the paramagnetic region which are due to a mineral of the chlorite series, which are aluminium silicates with various degrees of substitution on the cationic sites /Mn^{2+}, Fe^{2+}, Fe^{3+}/[12], and show up the presence of Fe^{2+} and Fe^{3+}.[8,11]. The peak at 0.2 mm/sec is the superposition of two peaks at least, one of each kind of iron atom. Data are compiled in Table 1 and have been obtained by visual reduction from the raw plotted data. The quoted errors are an estimate of the uncertainty of positions and widths, obtained through the drawing of a "best curve". The same three peak pattern is shown by the reddish sample, /Fig. 2/ with the important addition of a superimposed hyperfine spectrum whose parameters as found by calculation based on the four outer peaks are in Table 2. The parameters found for the magnetic hyperfine spectrum coincide with those of maghemite but do not exclude completely hematite[9,10]. The exact identity of the magnetic compound will be determined by Mössbauer spectroscopy studies at varying temperatures as to obtain the transition

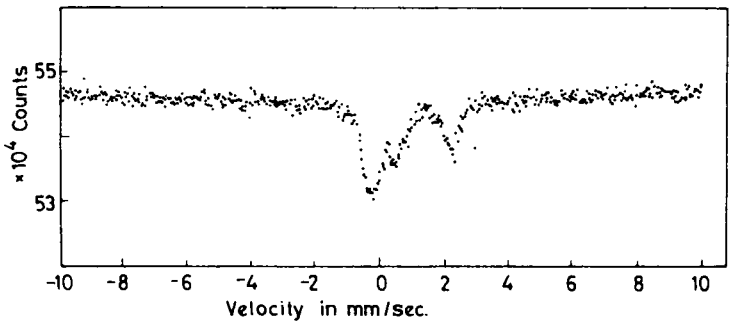

Fig.1. Mössbauer spectrum of the ochre sample at room temperature /see text/

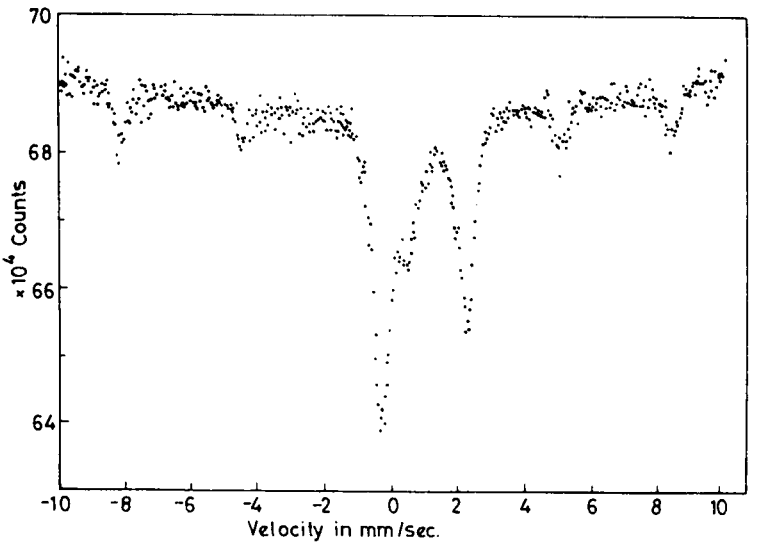

Fig.2. Mössbauer spectrum of the red sample at room temperature /see text/

TABLE 1

Peak No	I	II	III	IV	V	VI	VII
Sample	/positions in mm/sec/						
Red	-8.20±0.02	-4.54±0.06	0.29±0.02	0.46±0.02	2.25±0.04	5.02±0.02	8.28±0.04
Ochre	-0.2 ±0.1	0.5 ±0.04	2.26±0.04				

Peak positions in Mössbauer spectra taken at room temperature and referred to the ^{57}Co in Cu source. The peaks are labeled from left to right as they appear in the spectra.

TABLE 2

IS* /mm/sec/	ΔE/mm/sec/	H/kOe/
0.18 ± 0.08	0.20 ± 0.15	511 ± 5

*referred to a natural iron foil, 0.001" thick

Parameters for the magnetically split hyperfine spectrum for the red sample at room temperature

temperature. The ratios of the non magnetic signal of Fe^{2+}/Fe^{3+} in both samples are similar as can be deduced from the relative intensities of the peaks. Therefore total Fe^{3+} concentration /relative to Fe^{2+} concentration/ is higher in the sample with higher uranium content. It may be of interest to point out that the spectrum of the red sample is very similar to one obtained by Herzenberg on an Atlantic red clay[8,11].

We can conclude that the reduction of U/VI/ to U/IV/ could be produced by at least two mechanisms. The first, and main one, would be due to the action of bacteria, whose existence is supported by the pigmentation distribution which was found /taking into account that bacteria are supposed to live in media with low CO_2 concentrations/. Furthermore the uranium distribution which was found supports the idea of a transport and precipitation mechanism which implies the action of Fe^{2+} of the chlorites.

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REFERENCES

1. L.Rayleigh, Proc.Roy.Soc.,186A /1946/ 411.

2. N.Katayama, XXI Int.Geol.Congr.,Part XV /1960/ 7.

3. C.L.Christ, J.R.Clark, Am.Mineralogist, 45 /1960/ 1026.

4. C.A.Blacke, et al. J.Am.Chem.Soc., 78 /1956/ 5978.

5. P.B.Hosteler, R.M.Garrels, Econ.Geol. 57 /1962/ 137.

6. L.J.E. Hofer, S.Weller, Science, /1947/ 470.

7. H.Nicolli, Proceedings Vth Argentine Geological Congress, October 1972 /in press/.

8. C.L.Herzenberg, Mössbauer Effect Methodology, Vol.V, 209, I.J.Gruverman ed., Plenum Press, New York/1969.

9. V.I.Goldanskii, R.H.Herber, Chemical Applications of Mössbauer Spectroscopy, Academic Press, New York/1968.

10. N.N.Greenwood, T.C.Gibb, Mössbauer Spectroscopy, Chapman and Hall Ltd., London/1972.

11. C.L.Herzenberg, D.L.Riley, Development in Applied Spectroscopy, Vol.VIII, 277, E.L.Grove ed., Plenum Press, New York/1970.

12. H.Strunz, C.Tennyson, Mineralogische Tabellen, Akademische Verlagsgesellschaft, Geest and Portig, Leipzig/1970.