ALTERATION OF METAL IN CR2 CHONDRITES AS ANALOGUE FOR LONG TERM CORROSION PROCESSES: RAMAN STUDIES OF CORROSION RIMS

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Introduction: The long term repository of nuclear waste provides a big challenge for material science. The material has to be stored safely for a time frame of at least 10^5-10^6 years – something difficult to simulate in a laboratory environment. In France, fission products and minor actinides resulting from the reprocessing of spent nuclear fuel are incorporated in a nuclear boro-silica glass in steel containers.

These waste packages have to be stored in a clay-rich geological repository. To estimate the long term behaviour of this materials at the metal- clay interface, abundant metal grains in CR chondrites provide a good analogue. They allow to get insight into the corrosion processes of the steel container [1]. Since CR chondrites show alteration over the whole range from type 3 to 1, they allow the investigation of all steps in alteration of the materials [2, 3]. The physico-chemical environment of the parent body during the alteration is sufficiently similar to that expected in the disposal facility with a temperature range of 50 - 150°C, Water/Rock ratios of 0.4 – 1.1 and low fO₂ [1-4].

Earlier we reported first results of SEM and EMPA studies on samples from Rennazzo and Al Rais (CR2) and GRO 95577 (CR1) [5,6].

For an exact mineralogical characterization, we conducted micro-Raman analyses on these samples. Here we present the results for a part of a corroded metal grain in the Al Rais CR2 chondrite. This FeNi-grain is in direct contact to the phyllosilicate rich matrix and exhibits a broad (50 microns) rim of various layers of corrosion products. These are already visible in the SEM-BSE image (Fig.1), although similar density of the oxides and sulfides result in a low phase contrast. Element distribution images based on a grid of point measurements using EMPA of iron, nickel and sulfur (Fig.3) show two different layers of a Fe and S-rich phase with iron-rich layers in between.

Samples and Techniques: Micro-Raman studies were conducted at the Pierre Süe laboratory in CEA Saclay, using a Invia Renishawmicro-Raman instrument equipped with a NdYag laser (532 nm) [7]. Spacial resolution (beam spot size on sample surface) was 2 micron.

Results: The different phases also can be easily distinguished by their colors in the optical image used for operating the micro-Raman – the magnetites are pink-greyish in color, the sulfides orange (Fig.2).

The results are presented in Fig.4. Two groups of spectra can be identified: One showing a very strong band at about 670 cm^{-1}, with smaller features at 550 cm^{-1} and 300 cm^{-1}. These are characteristic features for magnetite [8]. A second group shows a strong double- feature at 360 cm^{-1} and 300 cm^{-1} similar to those of pyrrhotite [8]. On some zones a small band at 670 cm^{-1} indicates some magnetite that is mixed with the sulfide phases in the analysed volume.

Discussion: These findings correspond well with the elemental distribution images. The corroded metal grain is surrounded by alternating layers of magnetite and sulfide.

Only the thin, innermost sulfide layers does not appear in the distribution images.

The magnetites are similar among to each other in the inner corrosion rim (as are the sulfides). This mineralogical homogeneity indicates a stable physico-chemical environment during their formation.

The occurrence of distinct layers of different phases indicates a chemical heterogeneity at the same time – either of the fluid phases or as result of diffusion processes.
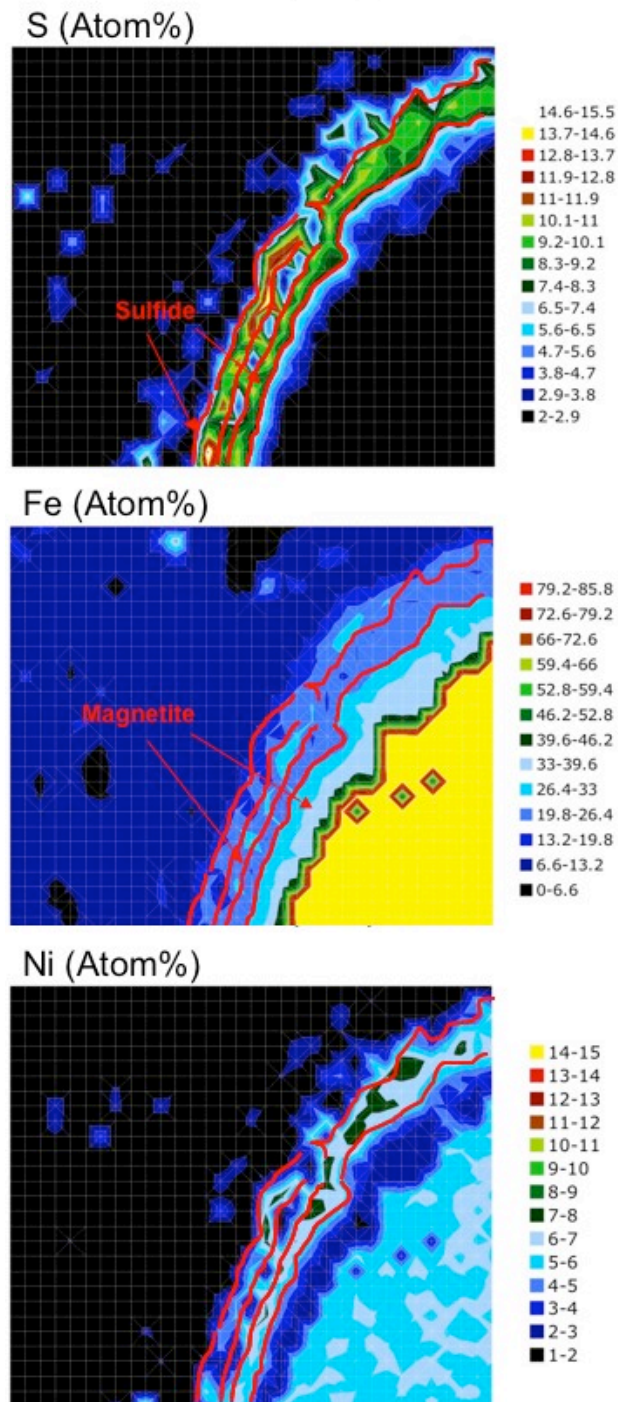
Conclusions and Future Work: Micro-Raman measurements is a suitable technique to identify very fine grained mineral phases in corrosion rims. Together future TEM analyses of the same rim sequence, it will be possible to estimate the physico-chemical parameters during the alteration of the metal.
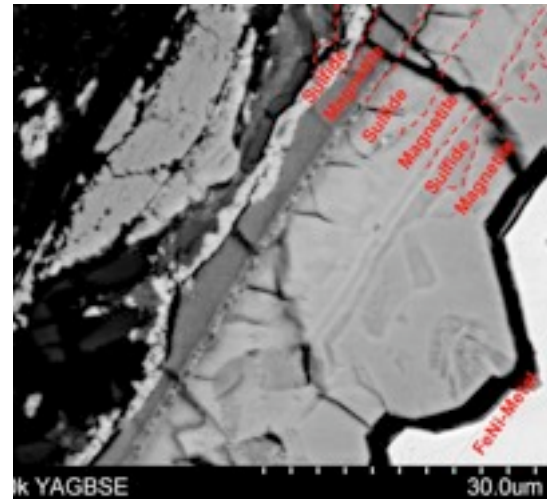

Fig.1: SEM-BSE image of the corrosion rim. The red dotted line helps to distinguish magnetites and sulfides.
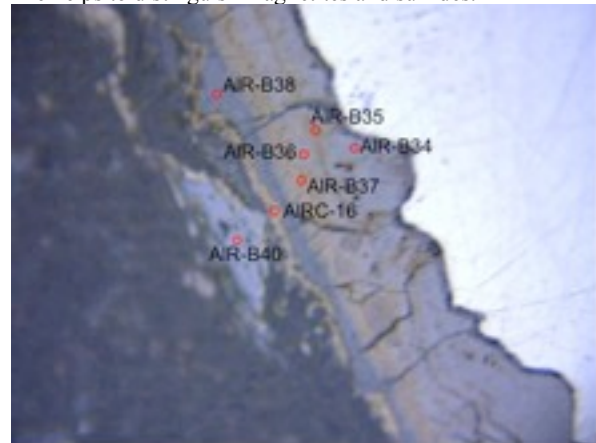
Fig.2: Optical image of the same area as in Fig.1. The red circles mark the spots of which Raman analyses were made.

S (Atom%)

	14.6-15.5
	13.7-14.6
	12.8-13.7
	11.9-12.8
	11-11.9
	10.1-11
	9.2-10.1
	8.3-9.2
	7.4-8.3
	6.5-7.4
	5.6-6.5
	4.7-5.6
	3.8-4.7
	2.9-3.8
	2-2.9

Sulfide

Fe (Atom%)

Magnetite

	79.2-85.8
	72.6-79.2
	66-72.6
	59.4-66
	52.8-59.4
	46.2-52.8
	39.6-46.2
	33-39.6
	26.4-33
	19.8-26.4
	13.2-19.8
	6.6-13.2
	0-6.6

Ni (Atom%)

	14-15
	13-14
	12-13
	11-12
	10-11
	9-10
	8-9
	7-8
	6-7
	5-6
	4-5
	3-4
	2-3
	1-2

Fig.3: Element distribution images of Fe, S and Ni (in Atomc%) for iron (based on EMPA-point grid analysis). The red lines show the sulfate rims.
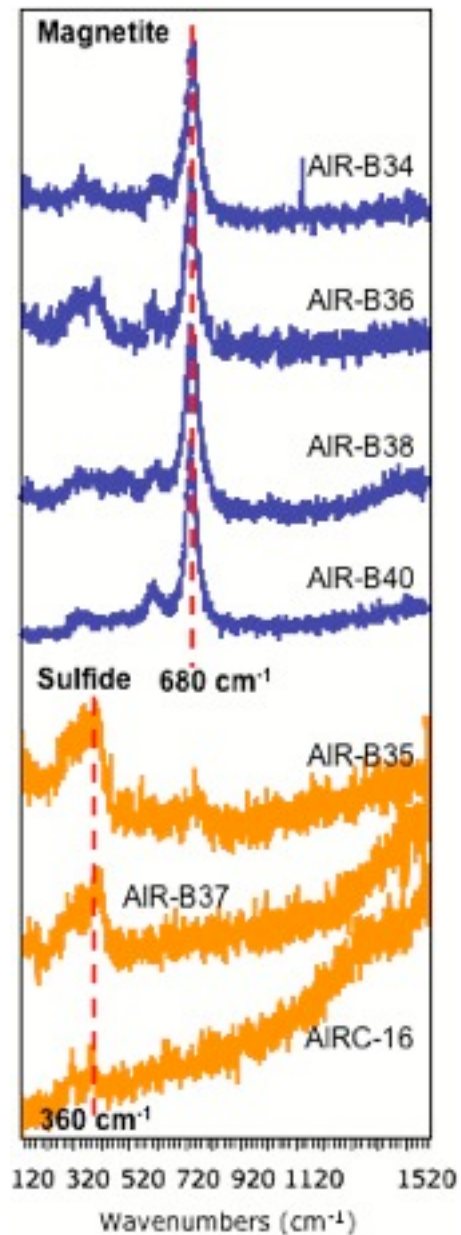
Fig.4: Raman spectra of the spots in Fig.2. Magnetites (top) are characterized by the band at 680 cm^{-1}, sulfides by the feature at 360 cm^{-1}.

References:
[1] Weisberg et al. 1993 *Geochimica et Cosmochimica Acta* 57, 1567 [2] Abreu 2007, PhD thesis [3] Weisberg M.K. and Huber H. 2007 *Meteoritics & Planetary Science* 42:9, 1495 [4] Zolensky, M. et al. 1993 *Geochimica et Cosmochimica Acta* 57, 3123 [5] Morlok and Libourel 2008 *Meteoritics & Planetary Science* 43:7, A104 [6] Morlok and Libourel 2008 *Meteoritics & Planetary Science* 43:7, A104 [7] Neff et al., 2006 *Journal of Raman Spectroscopy* 37, 1228 [8] Downs R. T. (2006) *19th General Meeting of the International Mineralogical Association in Kobe, Japan*. O03-13