Selenium and arsenic in sedimentary pyrites

M. Wolthers
P. R. van der Linde
C. H. van der Weijden

Department of Geochemistry, Utrecht University, P.O. Box 80021,
3508 TA Utrecht, The Netherlands

The redox-sensitive elements arsenic (As) and selenium (Se) can be used as indicators of palaeoredox conditions. In sediments, redox-sensitive elements undergo changes in their oxidation state during the transition from oxic to anoxic conditions, which affect their solubility (Table 1, and Fig. 1). The sedimentary cycling of both As and Se appear to be closely related to that of Fe. Iron sulphides, pyrite in particular, form an important sink for these trace elements in anoxic sedimentary environments.

The purpose of our study is to determine which reaction pathways lead to the incorporation of Se and As into pyrites, and to determine the reaction conditions underwhich incorporation takes place.

Background

The highest Se content of pyrites thus far reported in literature is 0.02 wt.%. Arsenic concentrations reported for pyrites range up to almost 0.93 wt.% for sedimentary and up 8 wt.% for hydrothermal pyrites.

While Se substitution for S within pyrite seems generally accepted, for As both cationic and anionic behaviour, and sub-microscopic inclusions of arsenopyrite in pyrite have been suggested. However, most evidence supports substitution of As for S.

Three different mechanisms can be envisaged for incorporation of As and Se into pyrite: (1) adsorption onto iron(II)monosulphides followed by incorporation during diagenetic conversion into pyrite; (2) direct adsorption and incorporation in the growing pyrite lattice; and (3) participation of dissolved As and Se species in the reaction of direct pyrite formation. The first two mechanisms will most likely occur during rapid pyrite formation, the latter during slow pyrite formation in a near equilibrium situation. Factors controlling these mechanisms are

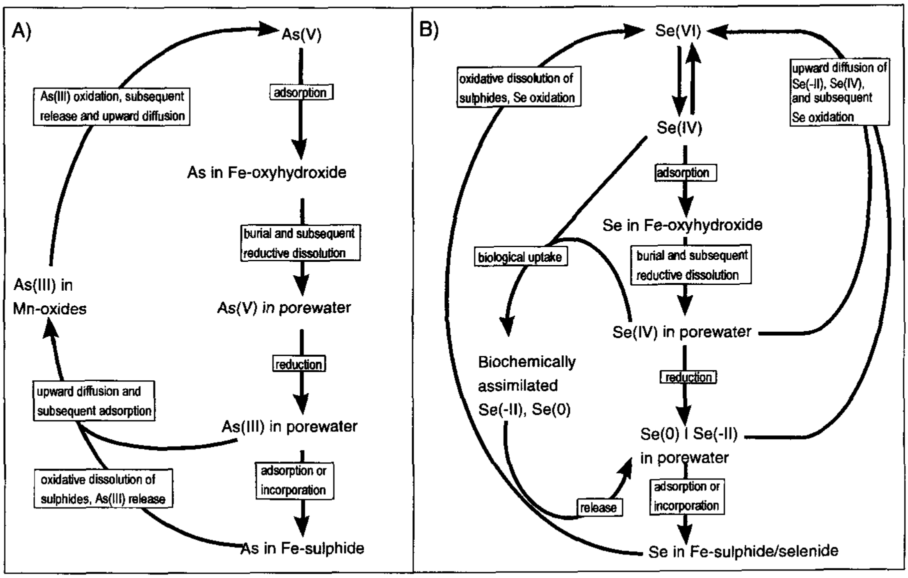

FIG. 1. Generalised sedimentary cycles for (A) arsenic and (B) selenium (based on Belzile (1988); Takayanagi and Belzile (1988); Mucci *et al.* (1998)).

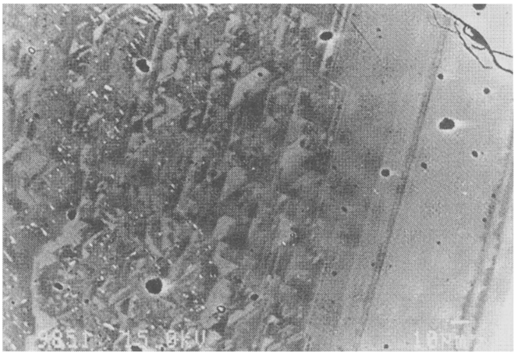

FIG. 2. Back Scatter Electron image of a pyrite sample. Light grey areas correlate with relatively As-rich zones within the sample, dark areas correspond to As-poor zones.

temperature, redox-potential and pH, and with these As and Se speciation, sulphide formation and Fe-oxyhydroxide reduction.

Experimental

In order to investigate Se and As concentrations and distributions in sedimentary pyrites, a microrobe study on natural pyrites is being performed. Preliminary results from a microprobe scan of a pyrite sample (Fig. 2) indicate a negative As/S correlation, suggesting substitution of As for S. At present it is not clear if the As distribution is an exsolution pattern or a growth-induced pattern.

TABLE 1. Some of the reduction reactions which can take place within a sediment with decreasing redoxpotential (Eh), (based on Masscheleyn and Patrick, 1994)

Eh (mV)	Reduction reaction
300 to 200	Se(VI) → Se(IV)
200 to100	As(V) → As (III)
100 to 0	Fe(III) → Fe(II)
0 to −100	Se(IV) → Se(0, -II)
−100 to −200	SO_4^{2-} → S(-II)

Future work will encompass synthesising pyrites in the presence of As and Se, while monitoring the speciation of S, Se, As and Fe using voltammetric methods. Subsequently, synthetic pyrites will be examined using electron microprobe analysis, and will be compared to natural pyrites studied.

References

Belzile, N. (1988) *Geochim. Cosmochim. Acta*, **52**, 2293–302.

Masscheleyn, P.H. and Patrick, W.H. (1994) *Biogeochemistry of trace elements, Sci. Techn. lett., Northwood*, 615–5.

Mucci, A., Richard, L-F., Lucotte, M. (1998) *1998 OSM*, OS95.

Takayanagi, K. and Belzile, N. (1988) *Mar. Chem.* **24**, 307–14.