Diverse origins of pyrites in Palaeoproterozoic uraniferous quartz-pebble conglomerates, Elliot Lake, Canada: Evidence from laser-microprobe sulphur isotope analyses

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Detrital *vs* hydrothermal origins of uraninite and pyrite

The occurrence of rounded grains of uraninite and pyrite in fluvial quartz-pebble conglomerates prior to 2.2 Ga has been used as the evidence for a low-O_2 atmosphere during the Archaean and the Palaeoproterozoic, because both minerals are readily oxidized under an oxidized environment. An alternative model, postulating hydrothermal mineralization of uraninite and pyrite (and associated gold), has been proposed based on detailed, structural and petrographical investigations of ores in the fluvial quartz-pebble conglomerates of the Witwatersrand Basin, South Africa (e.g. Barnicoat *et al.*, 1997). If this is the case, the survival of those 'detrital' minerals in this type of deposits may not be used as evidence for a low-O_2 atmosphere.

Sulphur isotopic compositions of sulphates and sulphides in sedimentary rocks have been used to reconstruct the palaeoenvironments during their formation. A wide variation in $\delta^{34}S$ values is a characteristic of pyrite formed by bacterial sulphate reduction. It has been reported that sulphides in continental sedimentary rocks of ~2.7 to ~2.2 Ga from Canada and South Africa have $\delta^{34}S$ values close to the mantle value (0 ‰) (e.g. Hattori *et al.*, 1983*a*). The small $\delta^{34}S$ variation of these samples appears to be consistent with detrital origin of pyrite in fluvial sedimentary rocks and thus consistent with a model of a low-O_2 atmosphere.

Recently, at least two types of pyrite grains have been recognized in ~2.4 Ga uraniferous quartz-pebble conglomerates of the Matinenda Formation at the Stanleigh mine, Elliot Lake, Canada (Mock and Ohmoto, 1997). The first type is grungy, altered, and often fractured pyrite grains: they may be either detrital and/or syngenetic in origin. The second type is clean, unfractured, and subhedral to euhedral pyrite grains: they appear to have been formed during and/or after diagenetic stages of host sediments. The second type is more common than the first type. Therefore, in order to identify the origins of various type of pyrite grains in ores at the Stanleigh mine, sulphur isotopic compositions of individual pyrite grains were analysed using a newly developed Nd-YAG laser microprobe method.

Results of sulphur isotope analyses by laser microprobe method

Sulphur isotope analyses were performed on single grains of pyrite of various size (~0.1 to ~2.7 mm diameter) and morphologies (euhedral, subhedral, anhedral, or rounded) that occur in a small rock chip (~1 cm^3 in volume: 73 analyses in total). A large variation in $\delta^{34}S$ values was found among these grains: a range of −9.0 to +5.5 ‰ with a mean value of $+0.6 \pm 2.1$ (1σ) ‰ (Table 1). More than 70 analyses of $\delta^{34}S$ values have been reported on bulk-rock pyrite samples from the Matinenda Formation: $\delta^{34}S$ values range from −1.5 to +1.2 ‰ with an average value of +0.2 ‰ (Hattori *et al.*, 1983*b*; Table 1). The mean $\delta^{34}S$ value for the single pyrite grains is, therefore, identical to that of the bulk-rock pyrite. However, the $\delta^{34}S$ range for single pyrite grains is much larger than that for the bulk-rock pyrite. There is no obvious correlation between the $\delta^{34}S$ values and the types of pyrite grains. However, it was noticed that the $\delta^{34}S$ values for larger pyrite grains are generally close to 0 ‰, but those for smaller grains tend to be more variable.

Discussion and interpretation

The observed large $\delta^{34}S$ variation is consistent with the recognition by Mock and Ohmoto (1997) of the presence of multiple types of pyrite. If all or most of the pyrite grains were detrital in origin, the $\delta^{34}S$ values of individual grains are expected to fall within a range of 0 ± 2 ‰, because the parental pyrite crystals, probably formed in igneous rocks (e.g.

granites, pegmatites) and/or in hydrothermal ore deposits (e.g. veins, massive sulphides of Archaean age), typically have $\delta^{34}S$ values within 0 ± 2 ‰.

The pyrite grains with $\delta^{34}S$ values within 0 ± 2 ‰ may include true detrital ones, but also include the ones formed *in situ* by other processes, such as syngenetic, diagenetic, and hydrothermal processes. Possible processes to generate pyrite grains with the observed $\delta^{34}S$ frequency pattern (i.e. the range of -9.0 to $+5.5$ ‰, the mean of $+0.6$ ‰, and the skewness toward negative values) may include: (1) bacterial processes during transportation of sediments in rivers (i.e. syngenetic sulphides) and/or during early diagenetic stage of host sediments; (2) involvement of low temperature (< 100°C) reduced fluids derived from a deep sedimentary basin; and (3) involvement of high temperature hydrothermal fluids of seawater origin. The details of the above processes are briefly discussed below:

(1) To explain the coexistence of pyrite grains of various morphologies and the occurrence of sulphur-rich kerogen in the 2.8–2.2 Ga uraniferous quartz-pebble conglomerates, Simpson and Bowles (1981) suggested the following 'bimodal' model: Partial oxidation of detrital grains of pyrite occurred to generate SO_4^{2-} and ferric hydroxides in the bedload by reaction with dissolved O_2 in river and pore water during transportation and deposition of the sediments. As a result, the bedload sediments became O_2-deficient, and enriched in SO_4^{2-} and ferric-hydroxides. Organic matter, remnants of algae and other organisms in sediments, were contained within the bedload of streams. Sulphate-reducing bacteria utilized the SO_4^{2-}, ferric hydroxides, and the organic matter to form syngenetic and early diagenetic pyrite. Some of the bacteriogenic H_2S was incorporated in the organic matter to form sulphur-rich kerogen. Reworking of these sediments containing both types of detrital and biogenic pyrite occurred. This scenario may also be applicable to some (or most) pyrite grains in the Stanleigh mine, because there are many lines of evidence suggesting that the 2.8–2.2 Ga atmosphere contained much more free oxygen than previously believed by many researchers (Ohmoto, 1997).

The $\delta^{34}S$ values of SO_4^{2-} formed by oxidation of detrital pyrite would have been ~0 ‰ because of small isotopic fractionation during oxidation of sulphides. Bacterial reduction of this SO_4^{2-} in closed systems with a kinetic isotopic effect ($\Delta_{SO_4^{2-}\text{-py}}$ value) of ~9 ‰ can explain the observed $\delta^{34}S$ frequency pattern. The magnitude of this $\Delta_{SO_4^{2-}}$-py value is not unreasonable at ~2.4 Ga.

(2) From a detailed textural study of U-Th-bearing minerals in the Stanleigh mine, Ono *et al.* (this volume) have suggested that most of uraninite in this deposit were formed by mixing of oxygenated groundwater and petroleum-bearing reduced fluid derived from a deep sedimentary basin. The reduced fluid may have transported H_2S of variable $\delta^{34}S$ values to form some (or most) of the pyrite grains in the deposit. Alternatively, the petroleum-bearing fluid may have contained appreciable amounts of SO_4^{2-}, much like modern basin brines, by dissolution of anhydrite in the sedimentary basin, and sulphate reducing bacteria may have utilized both the petroleum and SO_4^{2-} to form pyrite in the deposit.

(3) A close association of the second type (i.e. diagenetic/hydrothermal) of pyrite crystals with sericite in ore samples may suggest that these pyrite and sericite were formed by high temperature hydrothermal fluid. If the hydrothermal fluid was seawater origin and SO_4^{2-}-rich, thermochemical sulphate reduction by organic matter in the deposit could have formed pyrite with the observed $\delta^{34}S$ characteristics. This scenario, however, implies that the mineralization occurred after the district became submarine.

It is difficult to suggest which of the above three processes was most responsible for the formation of pyrite crystals in the pre-2.2 Ga uraninite deposits. Future analyses of sulphur isotopic compositions of other sulphide minerals, especially galena in uraninite crystals, and trace element characteristics of pyrite grains with variable $\delta^{34}S$ values and morphologies are expected to shed more light on the origins of pyrites in this type of deposits.

References

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