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$\delta^{34}\text{S}$ studies of pyrite generations related to uranium mineralizations at Osamu Utsumi Mine, Poços de Caldas Alkaline Complex, Brazil

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The Poços de Caldas Alkaline Caldera Complex, the largest one known in South America, is located in parts of southern Minas Gerais and São Paulo states, SE Brazil. It is subcircular and about 30 km in diameter, with an areal extent of 800 km² and is composed predominantly of leucocratic phonolites and nepheline syenites^{1,2,3}. The latest stage of the multi-stage magmatic evolution of the nephelinitic rock suite included strong but localized specific hydrothermal alterations associated with magmato-phreatic explosive activity, breccia pipe formation, generalized pyritization and hypogenic U-mineralizations of protore grade. Weathering processes acting since at least 76 Ma caused mainly pyrite oxidation and the development of spectacular redox fronts with secondary supergene U-enrichment and pyrite formation through roll-front type descendent processes^{4,5}. These processes led to the formation of ore-grade U-concentrations along with an ennobling of the ore due to the separation of the supergene U from its original hydrothermal association with high concentrations of Zr, Th and LREE.

In this study sulphur isotope analyses of pyrite generations and sulphates related to U-mineralizations contribute to a better understanding of hypogenic and supergenic U-metallogenesis and environmental migration of uranium.

Mineralogical, petrographical and ore-microscopical studies revealed characteristic differences between the hypo- and supergenic U-pyrite associations that allowed physical separation of the specific pyrite generations. Hydrothermal U-mineralization and related pyrites occur throughout the mass of hydrothermalized nepheline syenites, phonolites and magmatic breccias in two forms: (1) impregnated homogeneously in the rocks and rock fragments of the breccias and (2) irregularly enriched fracture mineralizations in the rocks and the breccia matrices and cements. The main U-mineral is highly crystalline, very fine grained (a few tens of microns) uraninite. Hydrothermal pyrites are predominantly idiomorphic and fine grained (several tenths to 1 mm); yet large, well developed crystals up to 10 and 15 mm are not rare. In the near vicinity of redox fronts hydrothermal pyrites are frequently rounded and corroded due to incipient dissolution and release of Fe(II) sulphate solution.

Supergenic U-mineralizations occur exclusively closely related to the redox fronts as millimetric to centimetric, frequently zoned, nodular pitchblende aggregates, irregularly and discontinuously distributed within zones generally less than 20 cm in width that extend immediately adjacent to the redox fronts on the reduced side. The main U-mineral of the pitchblende nodules is cryptocrystalline, frequently botryoidal uraninite of low crystallinity, as shown by SEM and X-ray diffraction studies. Secondary pyrite of the supergenic U-mineralizations occurs only inside the pitchblende nodules and is idiomorphic and coarser grained than the hydrothermal pyrites of the rock matrix.

Hydrothermal pyrites were separated as very pure concentrates from both rock matrices and fracture mineralizations. S isotopic measurements carried out at SURRC

based on conventional procedures⁶ on a mass spectrometer Isospec 44 modified for SO₂ revealed a very narrow range of $\delta^{34}\text{S}$ variation and no significant differences between the two texturally distinct types of hydrothermal pyrites. All the hydrothermal pyrites lie within the interval of +1.24 to -3.65 $\delta^{34}\text{S}\text{‰}$ (CDT).

Concentrates of pyrites from supergene pitchblende nodules were less pure due to inclusions of inherited pre-nodule hydrothermal pyrites. Nevertheless, all of the concentrates of secondary pyrites showed the lightest S-isotope compositions, ranging from -10 to -16 $\delta^{34}\text{S}\text{‰}$ (CDT). Individual larger sized crystals of secondary pyrites that could be separated from U-nodules according to net textural evidences and analyzed with laser beam techniques confirmed the lowermost $\delta^{34}\text{S}$ values. Finally, supergene K-Al and Fe(II)-Al sulphates (mainly kalinite and halotrichite) which formed under present-day atmospheric and climatic conditions on natural and artificial surfaces of hydrothermalized phonolites and nepheline syenites were separated and analyzed for their S-isotopic composition. They yielded results of +0.5 to -2.40 $\delta^{34}\text{S}\text{‰}$ (CDT), perfectly within the range of the hydrothermal pyrites of the same rocks.

Results show that the hydrothermal pyrites related to the hypogene high-temperature U-mineralization have S isotopic compositions compatible with an origin from upper mantle derived mafic magmas. Their compositional range is, interestingly enough, also the typical range of sulphides from porphyry copper deposits.

The low temperature secondary pyrites of the supergene pitchblende nodule have the isotopically lightest S, suggesting, as do the textural evidences, biological reworking of sulphur from hydrothermal pyrites and reprecipitation (sulphate-reducing bacteria) during the growth of pitchblende nodules related to redox front processes and water-table formation. U/Th disequilibria studies⁷ revealed growth rates of the pitchblende nodules of about 0.02 mm/ka, slower at least by a factor of 10² when compared to the rate of migration of local well-defined redox fronts (roll-front processes); these numbers are significant too for the supergene redox front related pyrite dissolution and its U-nodule related biogeochemical reprecipitation.

The variation of S-isotopical composition of supergenic sulphates within the range of the co-existing hydrothermal pyrites indicates complete oxidation of the pyrites in the presence of abundant oxygen without any isotopic fractionation.

References

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