

## Accessory (REE+Y)XO<sub>4</sub> phases: substitutions of As, S, Nb, Zr, Th, Ca and Sr in endogenous systems

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The solid solution systems of accessory (REE+Y)XO<sub>4</sub> phases with the monazite- or xenotime-type structure show a wide range of substitutions with apparent compositional variations of elements, especially As, S, Nb, Zr, Th, Ca, Sr in endogenous, magmatic to post-magmatic/ hydrothermal and metamorphic environments.

Sulphur, arsenic and niobium are commonly incorporated into REE, Y, Th-bearing phosphate (monazite, cheralite and xenotime) and silicate minerals (thorite, coffinite, huttonite) as sulphate (SO<sub>4</sub>)<sup>2-</sup>, arsenate (AsO<sub>4</sub>)<sup>3-</sup> and/or niobate (NbO<sub>4</sub>)<sup>3-</sup> anionic groups. The As, S and Nb content of these accessory minerals from common magmatic and metamorphic rocks is usually negligible. However, our investigation of various granites, rhyolites and metamorphic rocks revealed a systematic presence of As (up to almost complete monazite-gasparite, xenotime-cheronovite and partially thorite-cheronovite solid solutions), locally with increased S content (up to 8.4 wt. % SO<sub>3</sub>) as well as accompanying Ca or Sr (up to 7.4 wt. % SrO) and Nb constituent (up to 18 wt. % Nb<sub>2</sub>O<sub>5</sub>). The presence of Zr (up to 13 wt. % ZrO<sub>2</sub>) was documented in some intermediate solid solutions of the metastable system thorite-zircon-xenotime-(Y).

Small concentrations of S, As, Nb, Th, Ca as well as Sr in the (REE+Y)XO<sub>4</sub> phases of granitic and rhyolitic rocks seem to be a primary magmatic feature, whereas large contents of these elements indicate usually a subsolidus nature, probably due to post-magmatic, hydrothermal or metamorphic overprint of the primary rocks. These phases represent typical rock-fluid interaction products. The extensive incorporation of Zr into thorite originated probably as a product of partial late-magmatic to early subsolidus alteration and/or recrystallization of zircon, together with xenotime-(Y).

## Stage II of multiple-sulfur isotope records in South Africa

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Multiple-sulfur isotope records of the period between 2.09 and 2.45 Ga, is called Stage II, which is characterized by small non-zero  $\Delta^{33}\text{S}$  values (up to +0.5 ‰) and represents the transition from Archean mass-independent fractionation (MIF) to post-Archean mass-dependent fractionation [1]. The small non-zero  $\Delta^{33}\text{S}$  values of Stage II may reflect either input from oxidative weathering of Archean MIF continental sulfides, or atmospheric sulfur chemistry under an atmosphere with intermediate oxygen level [2].

We measured multiple-sulfur isotope ratios ( $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ , and  $\delta^{36}\text{S}$ ) of pyrite sulfur from the 2.41 Ga Koegas Formation and the 2.32 Ga Timeball Hill Formation in South Africa, in order to document multiple-sulfur isotope records of the Stage II by using improved high-precision analytical protocol [2]. The Koegas Formation yield MIF sulfides with  $\Delta^{33}\text{S}$  values up to +1.9 ‰, representing MIF sulfur from the youngest dated rock. The  $\Delta^{33}\text{S}$  values for pyrite sulfur in a series of drill cores of the Timeball Hill Formation range from +0.02 to +0.20 ‰, which is much narrower than previously reported values from Geophysical Laboratory [3]. The new range of  $\Delta^{33}\text{S}$  (determined by new high-precision protocol) is within that of Phanerozoic sulfides formed by mass-dependent (biological and hydrothermal) processes (e.g. [2, 4]). Our  $\Delta^{36}\text{S}$  data from the Timeball Hill Formation show  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios of -7.5, also supporting the mass-dependent origin of the small non-zero  $\Delta^{33}\text{S}$  values [2]. Therefore, there is no or very little signature of S-MIF in the 2.32 Ga Timeball Hill formation.

We conclude that the transition period between MIF and MDF is shorter than 90 million years. The level of seawater sulfate rose sufficiently high within 90 million years to dilute inputs of oxidative weathering of Archean MIF sulfide. This may imply that Proterozoic style sulfur cycle was established shortly after the deposition of the 2.41 Ga Koegas Formation.

[1] Farquhar & Wing (2003) *Earth Planet. Sci. Lett.* **213**, 1-13.

[2] Ono *et al.* (2006) *Geochim. Cosmochim. Acta* **70**, 2238-2252. [3] Bekker *et al.* (2004) *Nature* **427**, 117-120.

[4] Johnston *et al.* (2005) *Science* **310**, 1477-1479.