

The U-Pb in speleothem chronometer: Current progress and future prospects

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The chronology of speleothems by the U-Pb method has reached the point of a robust analytical methodology with enormous, but as yet largely unexploited, potential. A number of applications are beginning to appear relating to climate change, tectonics and human evolution. The next decade will likely see a major expansion of these activities. When coupled with other emerging technologies, the U-Pb chronology of speleothems from selected sites now has the potential to provide novel insights (both palaeotemperature and palaeohumidity) into ancient climate—effectively ‘ancient weather stations’—from around the globe and throughout much of Earth history. Meanwhile studies of included pollens and microscopic animals offer insights into floral/faunal diversity and change through geological time. The ramifications of these many developments will be significant across diverse fields of research, from human evolution, palaeontology and ecosystem development, through studies of weathering and erosion, to the influence of tectonics on landscape evolution.

Some solid solutions involving Fe₄O₅

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The recently discovered Fe-oxide phase with Fe₄O₅ stoichiometry [1] opens up the potential for this phase being stable in Earth's mantle. This is particularly the case since [2] demonstrated that magnetite breaks down to Fe₄O₅ + Fe₂O₃ at 9-10 GPa over a large range of temperature. Thus it is important to know if this new phase can incorporate other cations and form solid solutions which would expand its stability field in terms of P and T and composition. Experiments have been performed in 3 simple systems: i) Fe₃O₄-Fe₂SiO₄, ii) Fe₃O₄-(Mg,Fe)₂SiO₄, and iii) Fe₃O₄-FeCr₂O₄ over a P-T range of 9-16 GPa and 1100-1300°C.

The Fe₄O₅ phase essentially excludes Si, even when it coexists with stishovite or a Fe³⁺-bearing Fe₂SiO₄-rich spinel. The addition of Mg stabilizes a variety of assemblages in which the Fe₄O₅ phase occurs together with olivine, High-P clinopyroxene, spinelloid V, wadsleyite or ringwoodite. Experiments so far indicate solid solution of up to at least 25 mol % Mg₂Fe₂O₅ component. Molar volumes decrease from 53.76 to 53.55 cm³ mol⁻¹ over this solid solution range. Mg-Fe²⁺ partitioning is such that the Fe₄O₅ phase is the phase richest in Fe in a given assemblage, with $K_d^{\text{phase}/\text{Fe4O5}}$ usually <0.14. Cr can also be incorporated in the Fe₄O₅ structure in exchange for Fe³⁺. In the bulk compositions studied, the Fe₄O₅ phase coexists with a spinel and/or a hematite-eskolaite solid solution. Up to 0.92 cats. Cr p.f.u. have been measured so far, implying a Fe₂Cr₂O₅ component of 46 mol %. Molar volumes also decrease with increasing Fe₂Cr₂O₅ content.

[1] Lavina *et al.* (2011) PNAS, **108**, 17281-17285. [2] Woodland *et al.* (2012) Amer Mineral, **97**,1808-1811.