

## Crustal evolution of the Yangtze Block tracked by detrital zircons from sedimentary rocks

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The combination of U–Pb dating with Lu–Hf isotope analyses on detrital zircon grains from sediments is a powerful tool in identifying ancient crustal remnants and the origin of clastic sediments, and in providing an overview of Precambrian crustal reworking and growth.

Zircon U–Pb dating of sedimentary sequences from the Fanjingshan and Xiajiang Groups in the southeastern Yangtze Block show that they have similar depositional times and clastic compositions. Although formerly thought to be Mesoproterozoic, they consist dominantly of early Neoproterozoic detritus (0.9–0.8Ga) with minor Paleo- to Meso-proterozoic (2.0–1.5Ga) and Archean components (3.0–2.5Ga). The maximum depositional age of the basement sedimentary rocks in the Fanjingshan orogen is ca 0.8Ga, slightly younger than the adjacent Jiangnan orogen. The Neoproterozoic zircon grains may be subdivided into two groups based on Hf isotopic signatures. The first group has lower <sup>176</sup>Hf/<sup>177</sup>Hf ratios and mostly negative  $\epsilon_{\text{Hf}}(t)$  values; the second group has higher <sup>176</sup>Hf/<sup>177</sup>Hf ratios and positive  $\epsilon_{\text{Hf}}(t)$  values. Negative  $\epsilon_{\text{Hf}}(t)$  and Paleoproterozoic model ages for the first group of zircons suggest their sources experienced a long crustal history. Different Hf isotopic signatures in Neoproterozoic zircons from different formations suggest changes of source rocks. Most Mesoproterozoic zircons have positive  $\epsilon_{\text{Hf}}(t)$ , indicating a 'juvenile' or mantle-derived source. Both Paleoproterozoic and Archean zircons have low  $\epsilon_{\text{Hf}}(t)$ , indicating that their host magmas formed by reworking of older Archean crust.

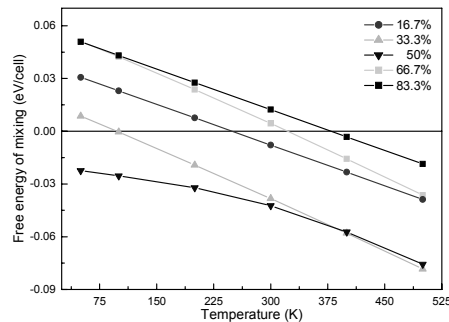
Paleoproterozoic and Archean crustal remnants with Archean model ages indicate that Archean basement is more widespread beneath the Yangtze Block than previously thought. Both recycling of ancient crustal materials and addition of juvenile crust took place at time intervals 2.5–2.4Ga, 2.0–1.7Ga, 1.6–1.4Ga and 0.9–0.8Ga during the Precambrian crustal evolution of the Yangtze Block.

## A computer simulation study of the thermodynamics of mixing in the (Ca, Mn)CO<sub>3</sub> solid solution

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The SOD (Site Occupancy Disorder) program [1] has been used to study the cation distribution in a single unit cell and a (2×1×1) supercell of the (Ca, Mn)CO<sub>3</sub> solid solution. Our results indicate that alternating Ca<sup>2+</sup> and Mn<sup>2+</sup> layers along the c-axis of the mixing system is favoured thermodynamically compared to any deviation away from this order. The (Ca, Mn)CO<sub>3</sub> solid solution is stable for the whole range of composition above 375K.



**Figure 1:** Free energy of mixing of the full range of Mn<sup>2+</sup> composition, as calculated for a single unit cell.

	S <sub>(300K)</sub>	S <sub>(800K)</sub>	S <sub>max</sub>	S <sub>∞</sub>
1×1×1	1.27	2.32	2.58	3.58
2×1×1	0.32	1.67	2.94	3.58

**Table 1:** Configurational entropies (10<sup>-4</sup> eV/K) per formula unit (Ca,Mn)CO<sub>3</sub> at 300 and 800K, compared to the values of a completely disordered system and infinite cell size.

The variation of configurational entropies of the (Ca, Mn)CO<sub>3</sub> solid solution shows cation ordering along the c-axis is only present below 800K, in agreement with previous calculations [2]. The configurational entropy calculated for the ordered (Ca, Mn)CO<sub>3</sub> structure is much lower than the completely disordered system, although another origin of entropy reduction is the periodic ordering imposed by the finite size of the employed supercell.

[1] Grau-crespo *et al.* (2007) *J.P. CM* **19**, 256201-256217.

[2] Victor *et al.* (2006) *Chem Geo* **225**, 304-313.