

## GEOCHEMICAL METHODS

Bulk diamictites and those containing malachite were lightly crushed and leached by 18MΩ water five times over one day period and supernatants collected. 2M HCl was added to the residue and shaken for hours before supernatants were collected. The sulfate in malachite was extracted from both water-treated and HCl-treated supernatants and was precipitated as barite. The HCl-treated residues containing barite were washed by 18MΩ water three times then treated with *diethylene triamine pentaacetic acid (DTPA)* to extract sulfate to be re-precipitated as pure barite. All initially precipitated barite were treated with DDARP method (Bao, 2006), a necessary step for purification of sulfate. The Cu<sub>2</sub>S in the acid and in the DDARP treated residues was extracted as Ag<sub>2</sub>S using a modified chromium reduction method (Canfield et al., 1986). The δ<sup>18</sup>O and δ<sup>17</sup>O of barite were simultaneously measured using laser-fluorination method to obtain the Δ<sup>17</sup>O for sulfate (Bao and Thiemens, 2000). The δ<sup>18</sup>O of barite was obtained using TCEA method. All the above experiments were done at LSU. The δ<sup>34</sup>S of BaSO<sub>4</sub> and Ag<sub>2</sub>S was analyzed at University of Maryland. The error bars for the δ<sup>18</sup>O and δ<sup>34</sup>S of sulfate are smaller than ±0.5‰ and ±0.3‰ respectively.

Table DR1. The δ<sup>18</sup>O, Δ<sup>17</sup>O, and δ<sup>34</sup>S for carbonate-associated sulfate in malachite (MAS) and barite in chalcocite clasts, the δ<sup>13</sup>C and δ<sup>18</sup>O for carbonates in malachite, and the δ<sup>34</sup>S for chalcocite in the Purple Shale Member of a Neoproterozoic diamictite, Kaiyang, central Guizhou.

Sample	δ <sup>18</sup> O-SO4 (VSMOW)	Δ <sup>17</sup> O-SO4	δ <sup>34</sup> S-SO4 (VCDT)	δ <sup>13</sup> C-CO3 (VPDB)	δ <sup>18</sup> O-CO3 (VPDB)
<b>Malachite patches</b>					
KY-08-1-1	-16.9	-0.35	-12.6	-11.3	-5.7
KY-08-1-2-HCl	-16.4	-0.06	-12.1	-11.2	-5.9
KY-08-1-2-W	-5.7	-0.11	-6.7		
KY-08-1-a-HCl	-17.6	-0.15	-8.6	-10.8	-6.2
KY-08-1-a-W	-0.4	n. a.	-8.7		
KY-08-1-b	-18.0	-0.20	-11.3	-7.4	-9.0
KY-08-1-b-g-W	-3.9	-0.11	-7.3		
KY-08-1-c	-16.1	-0.07	-10.6	-3.4	-11.1
KY-08-1-d	-18.7	-0.21	-10.9	-9.7	-6.5
KY-08-1-e	-17.3	-0.22	-9.9	-10.0	-7.0
KY-08-1-f	-17.7	-0.20	-9.8	-10.4	-5.7
KY-08-1-g				-6.0	-9.2

KY-08-1-h	-14.9	-0.18	-10.3	-2.9	-11.5
KY-08-1-h+i-W	-14.2	n. a.	-5.4		
KY-08-1-i	-8.3	n. a.	-5.7	-2.6	-11.5
KY-08-2-a	-9.5	n. a.	-6.0	-2.4	-11.2
KY-08-2-b	-9.5	n. a.	-8.5	-2.5	-11.8
KY-08-2-W	-2.0	n. a.	-3.2		
KY-08-3-HCl	4.1	n. a.	n. a.	-2.9	-13.1
KY-08-3-W	4.6	0.01	n. a.		

**Barite associated  
with chalcocite clasts**

KY-08-1-B	-18.9	-0.24	-11.7		
KY-08-1-1-B-1	-17.8	-0.22	-12.0		
KY-08-1-1-B-2	-17.4	-0.33	-11.7		
KY-08-1-1-B-3	-19.6	-0.19	-11.7		
KY-08-1-1-B-4	-17.9	-0.23	-11.7		
KY-08-1-b-B	-18.5	-0.26	-11.9		
KY-08-1-c-B	-17.5	-0.24	-11.0		
KY-08-1-d-B	-19.7	-0.21	-12.1		
KY-08-1-e-B	-18.8	-0.20	-12.1		
KY-08-1-f-B	-19.5	-0.20	-12.0		
KY-08-1-g-B	-20.3	-0.24	-10.7		
KY-08-1-h-B	-17.8	-0.18	-10.7		
KY-08-1-i-B	-14.5	-0.18	-9.7		
KY-08-2-a-B	-7.5	-0.21	-2.7		
KY-08-2-b-B	-6.1	-0.19	-3.2		

**Residual chalcocite  
(Cu<sub>2</sub>S)**

KY-08-1-1-Ag <sub>2</sub> S			-12.0		
KY-08-1-c-Ag <sub>2</sub> S			-12.1		
KY-08-1-d-Ag <sub>2</sub> S			-12.7		
KY-08-1-e-Ag <sub>2</sub> S			-11.7		
KY-08-1-f-Ag <sub>2</sub> S			-11.8		
KY-08-1-g-Ag <sub>2</sub> S			-10.6		
KY-08-1-h-Ag <sub>2</sub> S-1			-12.5		
KY-08-1-h-Ag <sub>2</sub> S-2			-12.1		
KY-08-1-i-Ag <sub>2</sub> S			-12.9		
KY-08-2-a-Ag <sub>2</sub> S			-12.8		
KY-08-2-b-Ag <sub>2</sub> S			-12.8		
KY-08-2-CuS-Ag <sub>2</sub> S			-12.7		

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Sample "KY-08-1" is a big piece of the diamictite containing chalcocite clasts and malachite seams; "KY-08-2" is a piece of diamictite 10 cm above "KY-08-1"; and sample "KY-08-3" is a piece of diamictite 15 cm above "KY-08-2". "W" stands for sulfate extracted by water only, while "HCl" for those further treated with 2 M HCl after water extraction. Most of the malachite

samples were from one single outcrop “KY-08-1”. The data show that  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  values of MAS are much higher for the water-extracted ones than for the HCl-leached ones.

### The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of Malachite

Multiple samples of malachite-bearing diamictite in the vicinity of chalcocite clasts yield a linearly inverse correlation between the  $\delta^{13}\text{C}$  and the  $\delta^{18}\text{O}$  of the bulk carbonates (Fig. 4), with one end-member characterized by low  $\delta^{13}\text{C}$  ( $-11.5\text{‰}$ ) and high  $\delta^{18}\text{O}$  ( $-5.8\text{‰}$ ) and the other by high  $\delta^{13}\text{C}$  ( $-3.5\text{‰}$ ) and low  $\delta^{18}\text{O}$  ( $-12\text{‰}$ ). The precipitation of malachite and its  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  space (Fig. DR1) offer an independent clue to the formation condition of malachite. The data in Fig. DR1 suggest an apparent two-component mixing between dolostone clasts in the diamictite and the authigenic malachite at the immediate vicinity of the chalcocite clasts. Because of the relative fractions of carbonates from the two sources are difficult to estimate, we can only conclude that the malachite end-member had a low  $\delta^{13}\text{C}$  (lower than  $-11.5\text{‰}$ ) and high  $\delta^{18}\text{O}$  (higher than  $-5.8\text{‰}$ ), which is consistent with those of carbonates precipitated in semi-arid continental environments (Cerling and Quade, 1993), a condition probably present during the oxidation of chalcocite clasts and the precipitation of at least some of the nearby malachite in the Kaiyang diamictite.

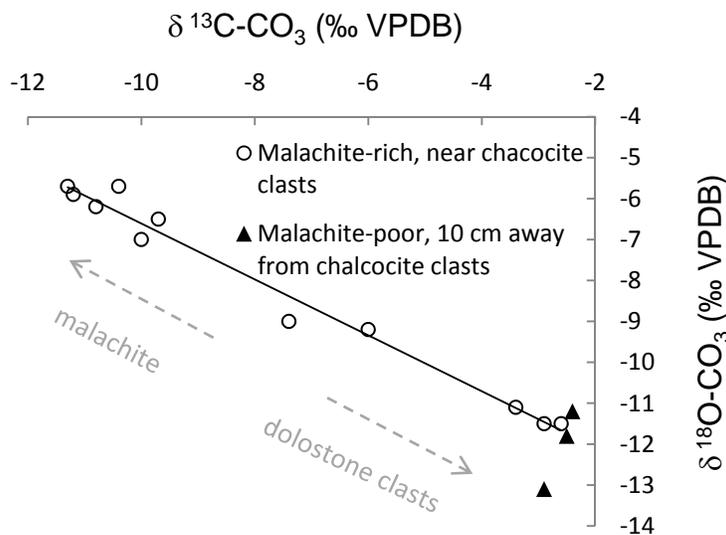


Figure DR1. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of multiple pieces of malachite-bearing diamictite in the vicinity of chalcocite clasts in the upper massive part of the Kaiyang diamictite, Guizhou, China. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of malachite were measured at Guangzhou Institute of Geochemistry, Chinese

Academy of Sciences. The standard deviation for the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of malachite are both smaller than  $\pm 0.1\%$ .

## References

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