

Geochronology and geochemistry of ore-bearing porphyries in the Lamasu and Dabate areas, western Tianshan (Northern Xinjiang, China)

G.J. TANG^{1,2}, Q. WANG^{1*}, Z.H. ZHAO¹, D.A. WYMAN³, Z.Q. JIANG^{1,2} AND X.H. JIA^{1,2}

¹Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China (*correspondence: wqiang@gig.ac.cn)

²Graduate School of Chinese Academy of Sciences, Beijing 100049, China

³School of Geosciences, Division of Geology and Geophysics, The University of Sydney, NSW 2006, Australia

The Lamasu and Dabate porphyry plutons are associated with copper mineralization located to the north of the Sayram Lake, west Tianshan (northern Xinjiang, China). The Lamasu pluton mainly consists of granodiorite, plagiogranite and diorite porphyries, but the Dabate pluton principally contains biotite-bearing granite porphyries. The Lamasu porphyries are calc-alkaline, and are mainly characterized by high Al₂O₃ (16.6-16.7 wt.%), Sr (308-444ppm) and Mg[#] (52-60) values, but relatively low Y (10.6-16.8 ppm) and Yb (1.21-1.60 ppm) contents, similar to subducted-oceanic crust-derived adakites. The Dabate porphyries are geochemically similar to A₂-type granites, e.g., high SiO₂ (75.6-77.6 wt.%), alkalis (Na₂O+K₂O= 8.27-8.70 wt. %) , low CaO (0.28-0.34 wt. %) and Mg[#] (1.8-10), distinctly negative Eu, Ba and Sr anomalies. Our new zircon LA-ICP-MS U-Pb age data suggest that the Lamasu adakitic porphyry and the Dabate A-type granite porphyry were generated at 366.3±1.9Ma and 288.9±2.3 Ma, respectively. We suggest that the Lamasu porphyries may be formed in island arc setting, related to Late Devonian subduction of the North Tianshan Ocean. However, the Dabate porphyries were likely emplaced in a post-collisional setting, related to post-orogenic lithospheric extension during the Early Permian. Taking into account Late-paleozoic tectonics^[1] and Carboniferous arc magmatism^[2, 3] in the northern Tianshan, we suggest that the Tianshan area was in an arc setting during the Late Devonian-Carboniferous, but evolved into a post-collisional stage in the Early Permian.

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[1] Xiao *et al.* (2006) *Acta Petrol. Sin.* **22**(1) 1062-1076.

[2] Wang *et al.* (2006) *Acta. Petrol. Sin.* **22**, 11-30. [3] Wang *et al.* (2007) *Chem. Geol.* **236**, 42-64.

Equilibrium Fe isotope fractionations in solutions

M. TANG AND Y. LIU*

State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China (Liuyun@mails.gyig.ac.cn)

Urey model or Bigeleisen-Mayer equation based theoretical method has been used to calculate the fractionation factors for almost all possible Fe-Cl, Fe-OH, Fe-NO₃ and Fe-HCO₃ species in solution. It includes almost all possible ferric and ferrous Fe monomer aqueous species, such as Fe³⁺, Fe²⁺, Fe^{III}Cl²⁺, Fe^{III}Cl₂⁺, Fe^{III}Cl₃, Fe^{III}Cl₄⁻, Fe^{II}Cl⁺, Fe^{II}Cl₂, Fe^{II}Cl₃⁻, Fe^{II}Cl₄²⁻, Fe^{III}OH²⁺, Fe^{III}(OH)₂⁺, Fe^{III}(OH)₃, Fe^{III}(OH)₄⁻, Fe^{III}(OH)₅²⁻, Fe^{III}(OH)₆³⁻, Fe^{II}OH⁺, Fe^{II}(OH)₂, Fe^{II}(OH)₃⁻, Fe^{II}(OH)₄²⁻, Fe^{III}NO₃²⁺, Fe^{III}(NO₃)₂⁺, Fe^{II}NO₃⁺, Fe^{III}HCO₃²⁺, Fe^{III}(HCO₃)₂⁺, Fe^{II}HCO₃⁺ and Fe^{II}CO₃, etc. The supermolecule clusters are used to precisely evaluate the solvation effects. At least 36 water molecules to be used to build the supermolecules. Up to 6 different conformers for each supermolecule are used to prevent the errors from the diversity of configurations in solution. The B3LYP/6-311G* level frequencies are then calculated for this study. Liu and Tossell [1] and Rustad *et al.* [2] have demonstrated that this supermolecule method could produce fractionation factors with the accuracy equal to experimental results.

Many of our results are different from the previous studies. For example, we find the fractionation between Fe³⁺(aq) and Fe²⁺(aq) in pure water is 3.5±0.2‰ at 22°C and 4.0±0.2‰ at 0°C. It is different from the previous studies. Our results will largely expand the database of Fe equilibrium isotope fractionation factors.

[1] Liu & Tossell (2005) *GCA* **69**, 3995-4006. [2] Rustad *et al.* (2008) *JPC A* **112**, 542-555.