

Fe³⁺ and Fe²⁺ partitioning among silicates in metapelites: A synchrotron micro-XANES study

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ABSTRACT

Synchrotron micro-XANES (X-ray absorption near-edge structure) spectroscopy (SmX) was used to measure Fe³⁺ and Fe²⁺ distribution among minerals in standard thin sections with an X-ray beam size of 10 × 15 μm. Measurements were made at beamline X26a, National Synchrotron Light Source, Brookhaven National Lab. Samples studied included metapelites from garnet to upper sillimanite zone rocks that coexist with graphite, graphite/ilmenite, or varying combinations of ilmenite, magnetite, and hematite. SmX results are compared with Mössbauer spectroscopic measurements of Fe³⁺ on mineral separates from the same rocks. Results show excellent agreement (within ±5–10%) between Mössbauer and SmX for the Fe-rich phases biotite, chlorite, staurolite, and garnet. Mössbauer spectra of muscovite typically show lower values than SmX for Fe³⁺/ΣFe (especially at low grades), suggesting contamination of the muscovite separates by fine-grained chlorite. However, heterogeneity of Fe³⁺ and Fe²⁺ is probably the chief source of discrepancy between the bulk and micro-scale measurements. The %Fe³⁺ (relative to total Fe) in these samples ranges from a high of 90% in muscovite to a low of 0–2% in garnet, with Ms > St = Bt = Chl > Tur > Grt in graphite/ilmenite-bearing rocks.

SmX measurements suggest that the averaged Fe³⁺/ΣFe in each mineral species does not change as a function of grade, but varies as a function of buffering assemblage, especially on a very localized scale. This effect shows that the oxygen buffering capacity of mineral assemblages is very large compared to the oxidizing/reducing potential of metamorphic fluids. However, distribution of Fe atoms among phases at each grade also reflects crystal chemistry. Across all grades, the Fe²⁺/Mg ratio is such that Grt >> St > Bt > Chl > Tur > Ms. Fe³⁺/Al is highest in biotite in garnet and sillimanite-zone rocks. For Fe³⁺/Al, Bt > Chl > Tur > St > Ms, and for Fe³⁺/Fe²⁺, partitioning behaves as Ms >> Bt ≈ St ≈ Chl > Tur > Grt in graphite/ilmenite-bearing rocks. Overall, partitioning of Fe³⁺ in any of the minerals of interest reflects both oxide assemblage and crystal-chemical constraints on the amount of Fe³⁺ that can be substituted into the structure.