Compositional Variation of Fe, Al, & F in Titanite

Bart J. Kowallis, Eric H Christiansen, Michael J. Dorais, Tony Winkel, Porter Henze, Lauren Franzen, and Haley Mosher – Brigham Young U.
Nakada, 1991

Fe (apfu)

Al (apfu)

- Central Andes Volcanics
- Granitoids
- Metamorphic
- High-P experimental

1:1 Fe/Al

1:2 Fe/Al
Conclusions – Fe/Al ratios

- The atomic ratio of Fe/Al in titanite from both volcanic and plutonic rocks is typically close to 1:1 and almost always >1:2.
- Volcanic titanite compositions typically cluster more tightly in terms Fe, Al, and F than do titanite compositions from any other environment.
- Fe/Al ratios in titanite from peralkaline silica-undersaturated volcanic and plutonic rocks are typically >1:1.
- Titanite from metamorphic, hydrothermal, and pegmatitic environments scatter widely in Fe/Al.
- Titanite from eclogite tends to have the lowest Fe/Al ratios, typically <1:8.
Conclusions – Charge Balancing

- Charge balance in metamorphic, hydrothermal, and pegmatitic titanite due to Fe$^{+3}$ and Al$^{+3}$ substitution into the Ti$^{+4}$ site is largely accomplished by the coupled substitution of F$^{-}$ for O$^{-2}$.

- However, in volcanic and plutonic titanite the charge imbalance due to Fe$^{+3}$ and Al$^{+3}$ substitution appears to be mainly coupled with REE$^{+3}$ and Y$^{+3}$ substitution into the Ca$^{+2}$ site with a more minor contribution from F$^{-}$ substitution.

- In Si-undersaturated rocks, substitution into the Ti$^{+4}$ site by Nb$^{+5}$ coupled with Fe$^{+3}$ is a major factor in charge balancing.
Data Base

- 8,100+ titanite analyses
  - Most include Fe and Al
  - A large number also include F

- ~4,800 analyses are from Brigham Young Univ. and Univ. of Utah microprobe labs

- ~3,300 analyses from literature
Element Substitutions

- Basic Formula = CaTi(SiO$_4$)(O,F,OH)

- Ti$^{4+}$-site elements = Al$^{3+}$, Fe$^{3+}$, Nb$^{5+}$, Ta$^{5+}$, V$^{5+}$, Zr$^{4+}$, etc.

- Ca$^{2+}$-site elements = REE$^{3+}$, Y$^{3+}$, Mn$^{2+}$, etc.
Fe versus Al in Titanite

Volcanic

(n=1634)

Plutonic

(n=3329)
Fe versus Al in Titanite

Silica Undersaturated

Metamorphic

(n=1579)

- All other metamorphic
- Eclogites & other high-P
- Mafic metamorphic
- Diana metasyenite, NY
Saima alkaline complex, China (Wu et al., 2016), all other data from BYU.
Fe versus Al in Titanite

Silica Undersaturated

Metamorphic

- All other metamorphic
- Eclogites & other high-P
- Mafic metamorphic
- Diana metasyenite, NY
Metasyenite Shear Zone
Bonamici et al., 2014

- Type 1: Wall rock
- Type 2: Shear zone
- Type 3: Vein
- Type 4: Xenoblastic
- Other
Fe versus Al in Titanite
Fe + Al versus F in Titanite
Al versus F in Titanite
Fe versus F in Titanite
Conclusions – Fe/Al ratios

- The atomic ratio of Fe/Al in titanite from both volcanic and plutonic rocks is typically close to 1:1 and almost always >1:2.
- Volcanic titanite compositions typically cluster more tightly in terms Fe, Al, and F than do titanite compositions from any other environment.
- Fe/Al ratios in titanite from silica-undersaturated volcanic and plutonic rocks are typically >1:2.
- Titanite from metamorphic, hydrothermal, and pegmatitic environments scatter widely in Fe/Al.
- Titanite from eclogite tends to have the lowest Fe/Al ratios, typically <1:8.
Conclusions – Charge Balancing

- Charge balance in metamorphic, hydrothermal, and pegmatitic titanite due to Fe$^{+3}$ and Al$^{+3}$ substitution into the Ti$^{+4}$ site is largely accomplished by the coupled substitution of F$^-$ for O$^{2-}$.

- However, in volcanic and plutonic titanite the charge imbalance due to Fe$^{+3}$ and Al$^{+3}$ substitution appears to be mainly coupled with REE$^{+3}$ and Y$^{+3}$ substitution into the Ca$^{+2}$ site with a more minor contribution from F$^-$ substitution.

- In Si-undersaturated rocks, substitution into the Ti$^{+4}$ site by Nb$^{+5}$ coupled with Fe$^{+3}$ is a major factor in charge balancing.