High-pressure and high-temperature synthesis of Fe³⁺- and Fe²⁺-rich armacolite

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Armalcolite, an Fe–Mg–Ti oxide mineral with composition of $(Fe_{0.5}Mg_{0.5})Ti_2O_5$ found at Sea of Tranquillity on July 20, 1969, is stable at low-pressure and high-temperature under low oxygen fugacity (cf. Anderson et al 1970; Kesson Lindsley 1975; Friel et al 1977). Miyake and Hokada (2013) reported ferric-rich acicular armalcolite with an X_{Mg} of 0.136 and $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ of 0.327 within porphyroblastic quartz in garnet–orthopyroxene-bearing quartzo-feldspathic gneiss

from Mt. Riiser-Larsen, in a terrane with the highest ultrahigh-teperature metamorphic grade in the Napier Complex, East Antarctica. Armalcolite is an important accessory mineral indicating a high-temperature paragenesis (e.g. Lindsley 1991) and would be a possible key mineral of the ultrahigh-temperature metamorphism.

The pure $(Fe_{0.5}^{2+}Mg_{0.5})Ti_2O_5$ is unstable below 1010 ± 20 °C at 1 atm (Lindsley et al 1974). The substitution of $Al^{3+}Al^{3+}$, $Cr^{3+}Cr^{3+}$ or $Ti^{3+}Ti^{3+}$ for $R^{2+}Ti^{4+}$ (where R^{2+} is a divalent cation) acts to stabilize armalcolite at lower temperatures (Kesson Lindsley 1975), and the incorporation of Fe³⁺ also reduces the temperature of armalcolite stability (Cawthorn Biggar 1993). The stability fields of armalcolite alone, a three-phase assemblage of armalcolite + ilmenite + rutile and a two-phase assemblage of ilmenite + rutile are divided by reaction boundaries with a positive dP/dT slope, indicating that the minimum temperature limit of armalcolite stability increases with increasing pressure (Friel et al 1977).



Fig. 1 Back scattered electron image (BSEI) of run products (run no. 140708) synthesised at 8 kbar 1100 $^{\circ}$ C for 87 hours in the Pt capsule from the mixture of ilmenite and rutile. Arm, armalcolite. Ilm, ilmenite. Rt, rutile.

The author has started high-pressure experiments to determine the stability field of armalcolite. In this meeting the preliminary experimental results will be reported on the stability of Fe³⁺- and Fe²⁺-rich armalcolite. Figure 1 shows the coexistence of armalcolite, ilmenite and rutile recrystallised from the mineral mixture of ilmenite and rutile in the Pt capsule at 8 kbar and 1100 °C for 87 hours. Under high oxygen fugacity, ferropseudobrookite Fe²⁺Ti₂O₅ component oxidizes to form rutile + pseudobrookite Fe³⁺TiO₅ (Anovitz et al 1985):

$$2Fe^{2+}Ti_{2}O_{5} + \frac{1}{2}O_{2} \rightleftharpoons Fe_{2}^{3+}TiO_{5} + 3TiO_{2}$$

$$Arm \qquad gas \qquad Arm \qquad Rt$$
(1)

and ilmenite 3Fe²⁺TiO₃ forms an armalcolite-pseudobrookite solid solution (Hayob Essene 1995):

$$3Fe^{2+}TiO_3 + \frac{1}{2}O_2 \rightleftharpoons Fe_2^{3+}TiO_5 + Fe^{2+}Ti_2O_5$$
Ilm gas Arm solid solution (2)

These indicate that if the oxygen fugacity increases, reactions (1) and (2) progress toward the right-hand side; consequently, the temperature of the stability field of armalcolite decreases with increasing oxygen fugacity.

References

Anderson et al 1970 Proc Apollo 11 Lunar Sci Conf 1 55–63 Anovitz et al 1985 Geochimi Cosmochim Acta 49 2027–2040 Cawthorn Biggar 1993 Contrib Mineral Petrol 14 221–235 Friel et al 1977 Geochim Cosmochim Acta 41 403–410 Hayob Essene 1995 Am Mineral 80 810–822 Kesson Lindsley 1975 Proc 6th Lunar Sci Conf 1 911–920 Lindsley 1991 Rev Mineral 25 69–106 Lindsley et al 1974 Geochim Cosmochim Acta 1 521–534 Miyake Hokada 2013 Eur Jour Mineral 25 33–38