DISCUSSION

The oxygen fugacity stability of deerite: an alternative view

A. I. OKAY, İTÜ, Maden Fakültesi, Jeoloji Bölümü, Teşvikiye, Istanbul, Turkey

The oxygen fugacity stability of deerite is discussed in a recent paper by Vernié, Kienast & Mével (1986). They describe a deerite-bearing rock from Corsica in which they interpret deerite to have formed under oxygen fugacities of the hematite/magnetite buffer. This contradicts the available data indicating that deerite is only stable under reduced conditions.

The rock described by Vernié et al. (1986) contains quartz, aegerine, iron oxides, sodic amphibole and deerite. Iron oxides include large magnetite crystals with thin rims of hematite, and bands of hematite/magnetite 'intergrowths'. The presence of hematite and magnetite in the rock is taken by the authors as evidence that deerite has formed under the oxygen fugacities of the hematite/magnetite buffer.

In addition to the iron oxides, other ironbearing minerals in the assemblage may place constraints on the f_{O_2} during the metamorphism. Aegerine is described from highly oxidising environments coexisting with hematite, and from highly reducing environments as an authigenic mineral coexisting with hydrocarbons (Milton & Eugster, 1959). Sodic amphiboles, however, with their independently variable Fe²⁺/Fe³⁺ ratios, are highly sensitive to the ambient f_{O_2} , and their compositions record the oxygen fugacities during their growth. The sodic amphibole field was emperically calibrated in terms of f_{O_2} using naturally occurring sodic amphibole-iron oxide pairs (Okay, 1980, Fig. 1). The sodic amphibole rim compositions from the Corsican blueschist fall well within the magnetite stability field in the calibrated sodic amphibole diagram (Fig. 1) indicating that the sodic amphibole rims formed under the oxygen fugacities in the magnetite field. Similarly all published sodic amphibole compositions from deerite-bearing rocks plot within the magnetite stability field on the sodic amphibole diagram suggesting that deerite is not stable at the magnetite/hematite boundary or hematite-field oxygen fugacities (Fig. 1). This is experimentally confirmed by Langer, Lattard & Schreyer (1977) who found no stability field for deerite with the magnetite/hematite buffer and could only synthesize it with the Ni/NiO buffer. In experimental runs with the magnetite/hematite buffer, Langer *et al.* (1977) obtained magnetite and quartz instead of deerite. In quartz-bearing

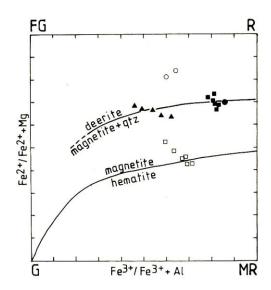


Fig. 1. Sodic amphibole compositions from deeritebearing rocks. (□) and (■) core and rim compositions of sodic amphibole from the Corsican rocks (Vernié et al. 1986). Other sodic amphibole compositions are—(▲) from Sifnos (Schliestedt, 1980); (•) from New Caledonia (Black, 1973); (0) from Shuksan (Brown, 1974). The magnetite/ hematite f_{O_2} isopleth is from Okay (1980). The compositon of sodic amphibole from Shuksan deviates from the deerite/magnetite + quartz f_{O} . isopleth, although it coexists with magnetite and deerite (Brown, 1974). This may be due to the higher temperatures of the Shuksan metamorphism. (G) glaucophane; (FG) ferroglaucophane; (R) riebeckite; (MR) magnesioriebeckite.

rocks this reaction between end-member deerite and magnetite constitutes an f_{O_2} buffer:

$$Fe_{12}^{2+}Fe_{6}^{3+}Si_{12}O_{40}(OH)_{10} + 1.5O_{2}$$
deerite
$$\rightleftharpoons 6Fe_{3}O_{4} + 12 SiO_{2} + 5H_{2}O \quad (1)$$
magnetite quartz

The oxygen fugacities defined by this buffer must be slightly more than the Ni/NiO buffer at which deerite was synthesized but less than the magnetite/hematite buffer. The location of the deerite/magnetite + quartz buffer on the sodic amphibole field is estimated from the composition of the sodic amphiboles coexisting with deerite, magnetite and quartz (Fig. 1). This oxygen fugacity isopleth provides an upper $f_{\rm O_2}$ limit for deerite, and its location, well within the magnetite field, again shows that deerite cannot coexist with hematite.

In quartz-bearing rocks deerite, aegerine, riebeckite and iron oxides lie to a first approximation in the Na–Fe–O system. Phase relations in this system also illustrate the incompatibility of deerite and hematite (Fig. 2). Thus reactions involving deerite and hematite, as given in Vernié *et al.* (1986) are metastable and do not occur in nature.

As pointed out by Vernié *et al.* (1986), the upper $f_{\rm O_2}$ stability of deerite may extend to higher values through the substitution of Mn and Mg for Fe²⁺ in the deerite structure.

Corsican deerite, however, shows minor substitution of Mn + Mg for Fe²⁺ (9%); sodic amphibole compositions coexisting with deerites of similar Mn + Mg contents (e.g., Schliestedt, 1980) indicate that such minor substitution does not increase the upper $f_{\rm O_2}$ stability limit of deerite to the magnetite/hematite oxygen fugacities.

The strong discontinuous zoning in sodic amphibole from the Corsican rocks indicates strong reduction during the metamorphism (Fig. 1, Okay, 1980). The core compositions of the sodic amphibole plot on the magnetite/hematite isopleth on the sodic amphibole field (Fig. 1), suggesting that hematite could once have been present in the rock. It was probably destroyed by a continuous reaction:

$$4NaFeSi2O6 + 3Fe2O3 + 8SiO2 \Leftrightarrow$$
aegerine hematite quartz
$$2Na2Fe32+Fe23+Si8O22 (OH)2 + 0.5O2 (2)$$
riebeckite

The riebeckite-rich rims probably formed at this stage. Further reduction, possibly due to the influx of hydrogen-bearing fluids, led to the formation of deerite through reaction (1) (Fig. 2).

Hematite in the Corsican blueschist is probably a result of post-metamorphic martitization involving the alteration of magnetite to hema-

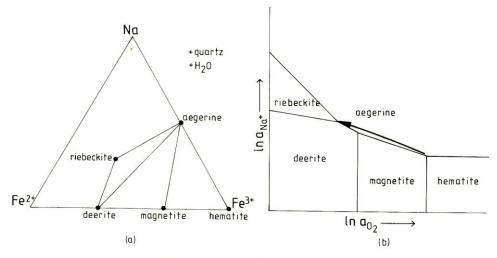


Fig. 2. a. Phase relations in the Na–Fe–O system illustrating the incompatibility of deerite and hematite. b. Chemical activity diagram in the same system. The arrow shows a possible path for the Corsican blueschist. The scale of the lna_{Na}^+ axis is exaggerated four times compared to the scale on the lna_{O_2} , axis. Note that although the upper f_{O_2} stability limit of the pure end-member riebeckite is less than that of deerite, naturally occurring riebeckite may have a similar or a higher f_{O_2} stability field compared to deerite.

tite. During the martitization hematite frequently forms thin oriented lamellae in magnetite giving the appearance of intergrowths (Ramdohr, 1969). Thin rims of hematite around large magnetite crystals are also reminiscent of martitization. In most described buffered assemblages hematite and magnetite occur as distinct separate crystals (e.g., Chinner, 1960).

Mineral assemblages of the deerite-bearing rocks, experimental work on deerite and theoretical phase relations analysis in the Na-Fe-O system indicate that deerite is only stable at oxygen fugacities below that of the magnetite/hematite buffer.

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