

ERRATUM

Solution calorimetric determination of the enthalpies of formation of NH₄-bearing minerals buddingtonite and tobelite by Guy L. Hovis,¹ Daniel Harlov,² and Matthias Gottschalk² (vol. 89, no. 1, pages 85–93, 2004).

The gram formula weights (gfw) of buddingtonite, tobelite, and salammoniac given in Hovis et al. (2004) are incorrect. This mistake, which also affected molar enthalpies of solution and formation, was generated on a spreadsheet used by the senior author to calculate the gfw values of minerals, where the summation of atomic weights inadvertently excluded the atomic weight of the one N atom each in the chemical formulae of buddingtonite (NH₄AlSi₃O₈), tobelite [NH₄Al₂(AlSi₃O₁₀)(OH)₂], and salammoniac (NH₄Cl).

Corrected average enthalpies of solution for buddingtonite (−598.1 ± 2.5 kJ/mol), tobelite (−935.0 ± 3.7 kJ/mol), and salammoniac (+11.23 ± 0.04 kJ/mol) have been determined by multiplying the original enthalpies of solution by factors equal to the correct gfw (257.2733, 377.2498, and 53.4916 g/mol, respectively) divided by the incorrect gfw given in Table 2 of Hovis et al. (2004). The enthalpies of formation for buddingtonite and tobelite at 323 K (the temperature of the HF solution calorimetric experiments) that result from the reaction schemes described by Hovis et al. (2004, p. 86) change to −3849.7 ± 0.4 and −5847.3 ± 3.6 kJ/mol, respectively (see revised Table 3). Adjustment of the latter data for temperature by +1.4 and +1.7 kJ/mol, respectively (see explanation in Hovis et al. 2004, p. 88), produce 298 K enthalpies of formation of −3848.3 ± 0.4 and −5845.6 ± 3.6 kJ/mol for the two minerals.

The estimates of room-temperature entropies (*S*) of buddingtonite and tobelite by Hovis et al. (2004, p. 89) based on the Δ*S* values of ion-exchange reactions were independent of enthalpy values and thus unaffected by these corrections. However, the 298 K entropies for buddingtonite and tobelite calculated by

combining the Gibbs free energies of formation of Mäder et al. (1996) with the corrected enthalpies of formation above now change to 178 and 309 J/(mol·K), respectively. Although closer than before to the expected entropy values of ~247 and ~319 J/(mol·K) for buddingtonite and tobelite, the entropy for buddingtonite, particularly, remains significantly lower than one would expect.

The 298 K Gibbs free energies of formation (from the elements) calculated by combining the corrected enthalpies of formation with the original 247 and 319 J/(mol·K) entropies (Hovis et al. 2004) for buddingtonite and tobelite are −3546 and −5386 kJ/mol, respectively. The new result for buddingtonite is 20 kJ/mol different from the value given by Mäder et al. (1996), but the value for tobelite is essentially indistinguishable, just 3 kJ/mol different, from the Gibbs free energy of formation given by the latter authors.

The phase equilibria given by Hovis et al. (2004) have been recalculated to check the effects of the corrected enthalpies of formation. Results, presented here as revisions of Figures 2 and 3 of the original paper, show that the various equilibria are lowered in temperature by 100 to 300 °C, which in turn limits the stability fields of buddingtonite and tobelite to upper-greenschist or lower-amphibolite facies, not granulite facies conditions. The failure of buddingtonite and tobelite to occur in lower-grade metamorphic rocks, therefore, could be related not only to low NH₃ contents, but also to slow kinetics at lower metamorphic temperatures. The revised equilibria, nevertheless, remain on the high-*T*/high-*X*_{N₂} side of the invariant point (see original Fig. 1) relative to equilibria based on the data of Mäder et al. (1996).

An additional correction should be made to Equations 10 and 11 of the original paper, each of which was missing the 0.5 coefficient to its N₂ term. This omission did not affect any of the reported calculations.

To conclude, there remain significant contrasts between

TABLE 3 (REVISED). Calculated enthalpies of formation at 323.15 K for buddingtonite and tobelite.

Reaction	Reactants	Products	<i>H</i> _{f(buddingtonite)}
A	Sanidine + Salammoniac	Sylvite + Buddingtonite*	−3849.5
B	Low albite + Salammoniac	Halite + Buddingtonite*	−3850.0
			<i>H</i> _{f(tobelite)}
C	Muscovite (ordered) + Salammoniac	Sylvite + Tobelite	−5857.4
D	Paragonite (ordered) + Salammoniac	Halite + Tobelite	−5863.5
E	Muscovite (disordered) + Salammoniac	Sylvite + Tobelite	−5842.2
F	Paragonite (disordered) + Salammoniac	Halite + Tobelite	−5847.2
G	Buddingtonite* (A above) + 2 Gibbsite	2 Water + Tobelite	−5849.6
H	Buddingtonite* (B above) + 2 Gibbsite	2 Water + Tobelite	−5850.0

* Buddingtonite enthalpy of solution adjusted by −3.78 kJ/mol by comparison of data for sample 0204 with those of sanidine (Hovis 1988).

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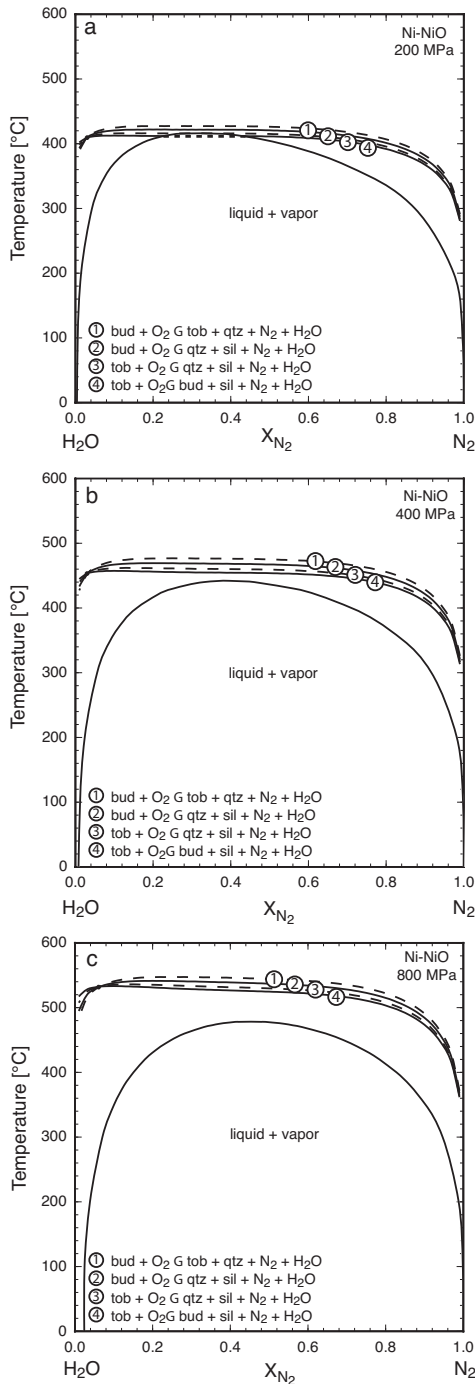


FIGURE 2 (REVISED). Revised calculations for equilibria 14–17 of Hovis et al. (2004) buffered to Ni-NiO oxygen fugacity plotted in T - X_{H_2O} - X_{N_2} space at 200 MPa (a), 400 MPa (b), and 800 MPa (c). Also plotted is the miscibility gap between N₂ and H₂O. Metastable equilibria (dashed lines) are written in smaller type. Tobelite entropy assumes Al-Si disorder. Relative to the original paper, the various equilibria are more compressed and lower in temperature by 100 to 300 °C. The same equilibria calculated from the data of Mäder et al. (1996), on the low- T /low X_{N_2} side of the invariant point, are shown in Figure 4 of the original paper.

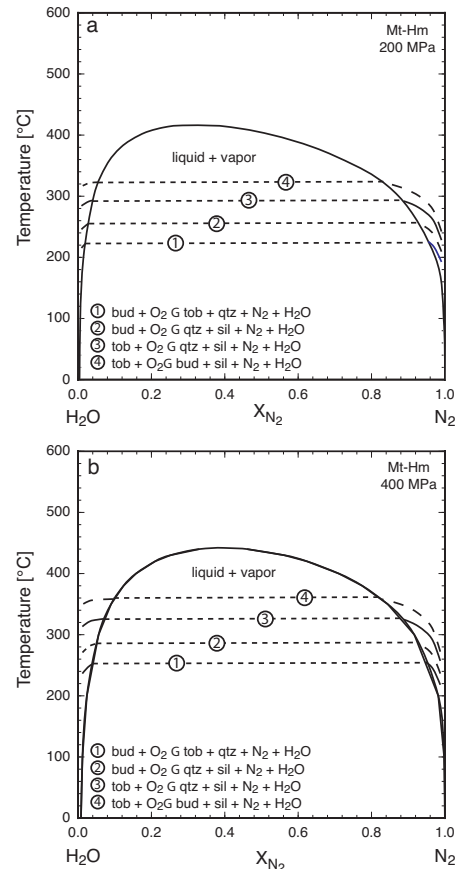


FIGURE 3 (REVISED). Revised calculations for Equilibria 14–17 of Hovis et al. (2004) buffered to Mt-Hm oxygen fugacity plotted in T - X_{H_2O} - X_{N_2} space at 200 MPa (a) and 400 MPa (b). Also plotted is the miscibility gap between N₂ and H₂O. Metastable equilibria (dashed lines) are written in smaller type. Tobelite entropy assumes Al-Si disorder. Relative to the original paper, the various equilibria are less compressed and lower in temperature by 100–200 °C.

the thermodynamic data for buddingtonite and tobelite given by this investigation vs. that of Mäder et al. (1996). Not only are there differences in the Gibbs free energies of formation of buddingtonite, but also there remains significant disagreement in the factoring of free energy into enthalpy and entropy for both buddingtonite and tobelite. The direct solution-calorimetric measurements of this investigation produce enthalpies of formation that are key to predicting reasonable phase equilibria for these NH₄-bearing minerals.

REFERENCES CITED

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