Heating experiments on gudmundite

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Summary. In the absence of published experimental data on phase equilibria in the ternary system Fe–Sb–S and on the stability relations of gudmundite (FeSbS) and berthierite (FeSb$_2$S$_4$), some preliminary investigations on the upper stability limit of natural gudmundite are briefly described. On heating in vacuo, As-free gudmundite broke down between 269° and 288° C, an approximate upper stability limit of 280±10° C conforming to the stability relations of the associated phases.

GUDMUNDITE forms rare prismatic euhedral crystals up to 3 mm in length encrusting siderite rhombs projecting into cavities in the wolframite–cassiterite–quartz veins of the Panasqueira tungsten deposit, Beira Baixa, Portugal (Thadeu, 1951). The gudmundite euhedra show the development of (?) (230) and (101) (Palache *et al.*, 1946), are untwinned, and are intimately associated with granules and platelets of monoclinic pyrrhotine (46·1–46·49 atomic % iron; Clark, 1965*a*). Gudmundite and monoclinic pyrrhotine were among the latest-formed minerals in the Panasqueira veins. Stibnite (with 0·13–0·14$_3$ wt. % iron, apparently in solid solution) occurs as a sporadic member of the earlier wolframite–cassiterite–quartz paragenesis (Clark, 1965*b*), and probably formed at temperatures approaching its melting-point (546° C), but it should be stressed that, in common with other W–Sn deposits in the Hercynian province, the Panasqueira assemblages are not significantly enriched in antimony.

Identification of the gudmundite was confirmed by X-ray powder diffraction and fluorescence analysis. Powder patterns taken with a diffractometer (Cu-*K*α radiation) and a Nonius Guinier–de-Wolff quadruple focusing camera (Co-*K*α; silicon as external standard) show no significant differences from that of the type gudmundite from Gudmundsdorp (Berry and Thompson, 1962). Elements other than Fe and Sb (e.g. As, Bi) were not detected by X-ray fluorescence analysis, but it is not known whether the specimens examined exhibit a deviation from stoichiometric FeSbS, a factor that might have appreciable effect on the stability relations of this mineral.

Separated gudmundite crystals were finely ground under acetone, and fractions were enclosed in evacuated rigid silica glass tubes, with minimal vapour space, and heated for different periods in horizontal 'Kullerud-type' electrically heated furnaces at temperatures between 139° C and 300° C. After annealing, the tubes were rapidly quenched

TABLE I. Selected heating experiments on gudmundite

Temperature	Duration	Products present on quenching
139° C	71 days	Gudmundite, unchanged
171	4	Gudmundite, unchanged
	33	Gudmundite, unchanged
245·5	40	Gudmundite, unchanged
269	72	Gudmundite, slight cell expansion
288	3	Gudmundite; pyrrhotine (hexagonal, presumably metastable); antimony
	19	Pyrrhotine (monoclinic+hexagonal); antimony
300	3	Pyrrhotine (monoclinic+hexagonal); antimony

in iced water and immediately examined on an X-ray diffractometer (Fe–$K\alpha$ radiation). No high temperature X-ray studies or d.t.a. experiments were carried out, but it is tentatively assumed that quenching was sufficiently rapid to prevent re-equilibration of the phases present. The results of the heating experiments are given in table I.

On the basis of these preliminary experiments it is suggested that gudmundite has an upper stability limit in the approximate range 270–290° C. Between 139° C and 245·5° C no changes were detected in the powder patterns of the gudmundite, but at 269° C minor shifts of the main reflections were observed, probably indicating a slight expansion of the cell. The pyrrhotine formed in the breakdown of the gudmundite showed asymmetrically split main reflections and comprised monoclinic and low-temperature hexagonal polymorphs. Neither pyrite nor berthierite formed in detectable amounts. Intergrowths of monoclinic pyrrhotine and gudmundite remained stable when heated for periods of up to 42 days at and below 269° C, and these phases probably constitute an equilibrium assemblage below that temperature. Pyrite is associated with the late-stage monoclinic pyrrhotine, but does not occur in contact with gudmundite in the Panasqueira assemblages. It should be stressed that the breakdown of gudmundite to pyrrhotine and antimony has not been reversed; gudmundite was not formed from intergrowths of the latter phases that were heated at 245·5° C for 55 days.

An upper stability limit of ∼ 280±10° C (at low confining pressures) for gudmundite is in broad conformity with the paragenetic relations

of this mineral in the Panasqueira and other deposits. Where gudmundite occurs in deposits exhibiting high-temperature characteristics it is generally restricted to the later stages of mineralization, as is the case at Panasqueira. The late-stage monoclinic pyrrhotine in the Panasqueira deposit is considered to be a primary phase (Clark, 1965a), and this pyrrhotine polymorph has been shown experimentally to have an upper stability limit of $308\pm5^\circ$ C at < 1 atm. (Clark, 1966). Confining pressures during mineralization have been estimated not to have exceeded 500–1000 bars (Clark, 1964), probably insufficient to markedly affect the stability relations of the pyrrhotine. Encrustation of the siderite crystals in the vein cavities, therefore, apparently took place below $\sim 308^\circ$ C, in permissive agreement with the proposed upper stability limit of the gudmundite. Furthermore, Seguin (1965 and personal communication) has demonstrated that the assemblage siderite–pyrrhotine–pyrite–vapour is stable only below ~ 340–365° C.

In an (unpublished) experimental investigation of the Fe–Sb–S system, N. L. Markham (written communication, 1964) has been unable to synthesize gudmundite under dry conditions at 600° C, 500° C, 400° C, and 330° C, charges having the stoichiometric FeSbS bulk composition yielding pyrrhotine and antimony at these temperatures. If equilibrium was attained at 330° C, these results indicate that gudmundite may only be a stable phase below $\sim 300^\circ$ C, in agreement with the conclusions of the present study.

References

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