

## SHORT COMMUNICATIONS

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### Oxygen isotope fractionation between cassiterite and water

ANALYSIS of stable isotopes in coexisting minerals has found wide application in the study of hydrothermal mineral deposits, particularly for elucidating the temperature and source of the fluid phase involved in mineralisation. For these purposes the temperature dependence of isotopic fractionation in several mineral-water systems has already been established (e.g. Friedman and O'Neil, 1977; O'Neil, 1986). Unfortunately, the oxygen isotope fractionation between cassiterite ( $\text{SnO}_2$ ) and water has not been adequately characterized, and this has hindered a full utilization of oxygen isotope data derived from studies of tin deposits (e.g. Harzer, 1970; Patterson *et al.*, 1981; Kelly and Rye, 1979). Because of this situation, an attempt is made here to derive a relationship between temperature and the fractionation of oxygen isotopes ( $\Delta$ ) between quartz and cassiterite, based on the fractionations observed in naturally-occurring assemblages and independent temperature estimates.

*Previous studies.* There have previously been several attempts to establish the relationship between temperature and  $\Delta$  for systems containing cassiterite and either quartz or water (here-with abbreviated *c*, *q*, and *w* respectively). These have either been unsuccessful (e.g. Matthews, 1973), or have produced only approximate or contradictory results (e.g. Borshevskii *et al.*, 1979a; Sushchevskaya *et al.*, 1986).

There are three possible approaches to the problem (Clayton, 1981):

- (1) By theoretical considerations, utilizing the differences in vibrational frequencies of the coexisting phases.
- (2) By synthesis of  $\text{SnO}_2$  in the laboratory and direct analysis of the coexisting cassiterite and water.
- (3) Empirically, by analysis of natural assemblages (and assumption of isotopic equilibrium).

(1) The theoretical approach uses the differences

in vibrational frequencies in the atoms of coexisting minerals and/or water as a measure of isotopic fractionation (O'Neil, 1986). This can be a complex exercise and has not been fully investigated in cassiterite-bearing systems. An indication of this approach and the results obtained for various silicates, calcite, and rutile can be found in the study by Kieffer (1982). Simpler approaches utilize heat capacity and spectroscopic data as measures of isotopic fractionation between minerals. For example, an approximate relationship between temperature and  $\Delta(q,c)$  can be obtained from the data of Golyshev and Padalko (1979). This relationship is shown in Fig. 1 and compares reasonably well with the suggestions by Hattori and Halas (1982), based on spectroscopic data, that  $\Delta(q,c)$  will be in the range 8–12‰ at temperatures between 270 and 300°C. Broecker and Oversby (1971) have also proposed a simplified method for investigating isotopic fractionations based on heat capacity data. Although their results show that the approach may be valid for silicates at high temperatures, it does not work for the quartz–cassiterite pair (cf. Patterson *et al.*, 1981). Over the temperature range of interest the calculations lead to geologically-unreasonable negative  $\Delta(q,c)$  values.

(2) Matthews (1973) attempted to calibrate the  $\text{SnO}_2$ - $\text{H}_2\text{O}$  system in the laboratory. He synthesized  $\text{SnO}_2$  by crystallizing stannic hydroxide and by the oxidation of Sn metal in steam. Neither of these approaches was successful—the first reaction was too rapid for equilibrium to be attained, and the second gave low yields or produced anomalous results. Sushchevskaya *et al.* (1986) also investigated this system by synthesizing  $\text{SnO}_2$  from Sn metal and dilute HCl. Their results indicated that  $\Delta(q,c)$  was close to zero per mil (0 to -1) in the temperature range 300–450°C. This is in marked contrast to the earlier plots produced by Borshevskii *et al.* (1979a, b) which indicated

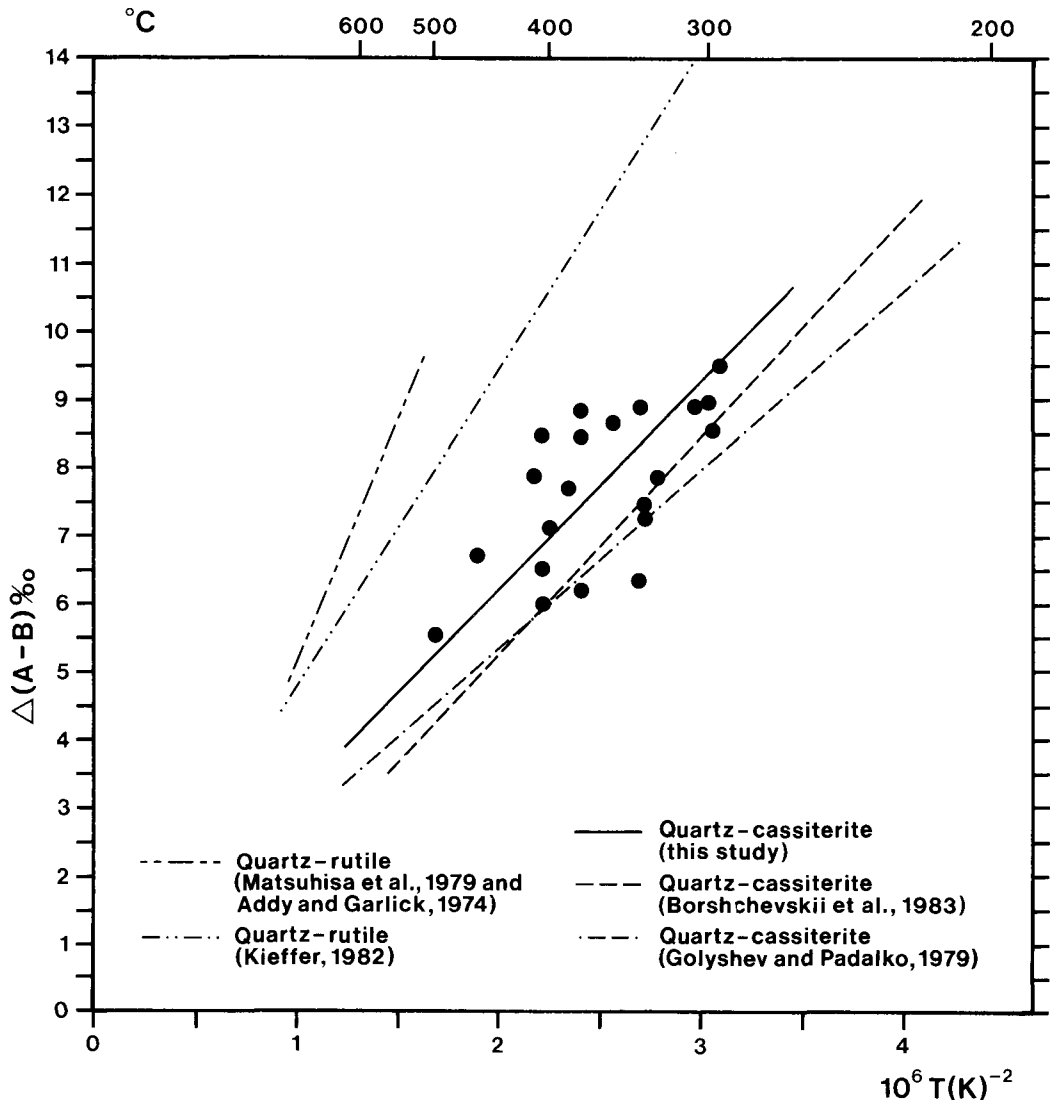


FIG. 1. Proposed oxygen isotope fractionation between quartz and cassiterite as a function of temperature. Individual data points used in the regression were taken from the results of Alderton (1976), Borshchevskii *et al.* (1979b), Mu Zhigo *et al.* (1982), and Sun and Eadington (1987). The fractionation relationship suggested by Borshchevskii *et al.* (1983) and the one derived from the spectroscopic data of Golyshev and Padalko (1979) are also shown. Also shown are the fractionations between quartz and rutile from Addy and Garlick (1974), Matsuhisa *et al.* (1979), and Kieffer (1982)

that  $\Delta(c, w)$  was *c.*  $-12\text{‰}$  at  $300^{\circ}C$  (and which incidentally led to complicated arguments explaining how Sn-rich fluids with  $\delta^{18}O > +15\text{‰}$  could be generated).

(3) Several studies have used analyses of natural assemblages to estimate the isotopic fractionation. For this the temperatures have been calculated independently from either fluid inclusions

or other stable isotope pairs. Thus Andrew *et al.* (1987) suggested that  $\Delta(q, c)$  is approximately  $9\text{‰}$  at  $300\text{--}400^{\circ}C$ , and Patterson *et al.* (1981) proposed it is  $8\text{--}12\text{‰}$  over the same temperature interval. Although not apparent from the literature, Borshchevskii *et al.* (1979a, b) presumably also used this approach to derive a relationship, and thus classify Sn deposits of the USSR. This was later presented by Borshchevskii *et al.* (1983)

as  $\Delta(q, c) = 3.25(10^6)(T^{-2}) - 1.26$  (where  $T$  is in  $^{\circ}\text{K}$ ).

**Present study.** As the relationship derived by Borshchevskii *et al.* (1983) did not agree with studies by the author in S.W. England, or with those of Sun and Eadington (1987) in New South Wales, it was decided to re-investigate all available oxygen isotope analyses of coexisting quartz and cassiterite and develop a temperature against  $\Delta(q, c)$  equation, using the empirical approach outlined in (3). Twenty-one O-isotopic analyses of quartz-cassiterite pairs were found in the literature from which  $T$  could be estimated (mostly isotopically, using co-existing quartz, muscovite, chlorite, or wolframite). Although temperatures derived from fluid-inclusion data are available from some studies, these have not been used because they usually represent minimum (homogenization) temperatures and are uncorrected for pressure effects. The magnitude of this correction is usually unknown but may be of the order of 50–100 $^{\circ}\text{C}$ . In addition some of the Soviet fluid-inclusion results have been obtained by decrepitemetry, a technique not altogether suitable for accurate temperature determinations.

Although isotopic equilibration between coexisting minerals cannot always be demonstrated, it is presumed that deviations in  $\Delta(q, c)$  from the true values for a particular temperature will not be consistently biased, and that regression of data from several different deposits should provide a meaningful calibration. The available data were subjected to linear regression, with the added proviso that the resulting straight line passed through the origin (i.e.  $\Delta(q, c)$  approaches zero at high temperatures). The equation for the line is:

$$\Delta(\text{quartz, cassiterite}) = 3.08(10^6)(T^{-2}) \quad (T = ^{\circ}\text{K})$$

This line, and the raw data from which it was derived are shown in Fig. 1. The line is not a perfect fit, pointing to a lack of complete isotopic equilibrium in assemblages containing quartz and cassiterite. This confirms the results of fluid inclusion studies by Jackson and Rankin (1976) and Moore and Moore (1979) who noted that apparently co-existing quartz and cassiterite formed from fluids of different temperature and salinity. However the spread of data points is such that the majority plot within  $\pm 60^{\circ}\text{C}$  of the line and so it is presumed to be a good approximation of the isotopic fractionation between quartz and cassiterite.

Also shown in Fig. 1 is the quartz-cassiterite fractionation proposed by Borshchevskii *et al.* (1983). This has a similar form to the relationship suggested here but for a particular value of  $\Delta$  gives temperatures *c.* 50 $^{\circ}\text{C}$  lower. Fractionations for

quartz and  $\text{TiO}_2$  are also plotted from the data of Kieffer (1982), Addy and Garlick (1974), and Matsuhisa *et al.* (1979). Clearly, oxygen isotopic fractionation between quartz and cassiterite is very different to that of quartz and rutile (cf. Patterson *et al.*, 1981).

Combining the proposed fractionation with the quartz-water fractionation of Matsuhisa *et al.* (1979) suggests that  $\Delta(c, w)$  is fairly constant at *c.* -2.5‰ over the range of geologically relevant temperatures (250–500 $^{\circ}\text{C}$ ). As the highest  $\delta^{18}\text{O}$  values for cassiterite are around 7‰ the heaviest fluids responsible for tin mineralization had  $\delta^{18}\text{O}$  around 9.5‰, a value close to that of magmatic fluids. As previously noted by Borshchevskii *et al.* (1983), temporal variations in  $\delta^{18}\text{O}$  for cassiterite must therefore be due to variations in fluid composition rather than temperature effects. In many tin deposits a lowering of O-isotopic values is noted in the younger episodes of mineralization, and this is most reasonably explained by an increased incorporation of isotopically lighter (probably meteoric) fluids into the hydrothermal system.

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## Högbomite from the Aldan Shield, Eastern Siberia, USSR

HÖGBOMITE, a complex oxide of Al, Fe, Mg, and Ti, is an important constituent of some iron ores and emery deposits as well as an infrequent accessory in aluminous high-grade rocks (e.g. Grew *et al.*, 1987). The recent increase in reports of new localities (e.g. Rammlmair *et al.*, 1988) suggests that högbomite may be more widespread than is generally perceived. We report here högbomite from the Aldan Shield, Eastern Siberia. This högbomite is remarkable for the wide variation in composition measured in a single thin section. Our report is only the second from the USSR of högbomite for which chemical data are given. Reports of högbomite other than Moleva and Myasnikova's (1952) well-documented descrip-

tion of högbomite from the Urals are based only on optical properties (Bobrovnik, 1955; Sinita, 1957; Sudovikov *et al.*, 1962); the third citation includes mentions of högbomite in pelitic gneisses from unspecified localities in the Aldan Shield. In the present paper we present details of the paragenesis and chemistry of högbomite and several associated minerals; the reader is referred to Drugova *et al.* (in press) for a general account of the högbomite-bearing rock and its geological and geochemical significance.

Högbomite is found in a biotite-plagioclase-corundum-spinel schist cropping out 2 km east of the Aldan River at a point 1 km north of its tributary Ayyannaakh Creek (approximately 120 km