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GEOCHEMISTRY OF THE HYDROTHERMAL DICKITE (NOWA RUDA, LOWER SILESIA, POLAND): CHROMIUM

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Abstract

Geochemical analyses for trace Cr have been made on a representative sample of a typical hydrothermal dickite filling vein at Nowa Ruda. The mineralogy of the sample is comparatively simple, dickite being the principal component (ca. 91% of total sample). Geochemical fractionation and inductively coupled plasma-optical emission spectrometry (ICP-OES) indicate that most (>96 % of total metal) of Cr reside in the dickite. The combination of geochemical and spectroscopic tools applied on Cr^{3+} allow one to specify the Eh (>0.4 V, highly oxidizing) and pH (≤4.0, highly acidic) of the solution during the formation of dickite from the Nowa Ruda Basin. We suggest that hot hydrothermal waters leached the surrounding varieties of gabbroids enriched in Cr for the dickite-forming solution.

Introduction

Acid alteration in magmatic hydrothermal systems is often represented by kaolinite group minerals including kaolinite, dickite, nacrite and halloysite [1]. Hydrothermal dickite is mainly formed in situ through alteration of source minerals (mainly K-rich feldspars and other aluminosilicates) by hydrothermal acid waters. Geochemical studies indicate that Cr occurs in natural aquatic environments in two oxidation states: Cr(III) and Cr(VI). In low (suboxic/anoxic) Eh natural environments, the main aqueous Cr(III) species are Cr^{3+} and $\mathrm{Cr(OH)}^{2+}$. Under oxidizing conditions, aqueous Cr is present in a Cr(VI) anionic form, HCrO_4^- and/or Cr_4^{2-}, depending on the pH. Cationic Cr(III) species are rapidly and strongly adsorbed by colloidal clay particles, but adsorption of anionic Cr(VI) species onto these particles is expected to be minimal [2, 3]. The hydrothermal dickites are not frequently studied and our knowledge of the physicochemical conditions necessary for their formation is still obscured. One way to get an objective evaluation of the nature of solutions during the formation (precipitation) of dickites is to examine components that undoubtedly were introduced into their lattice by these solutions. Such component is, for certain, Cr^{3+} ion.

Experimental

Sample location and description

The Nowa Ruda Basin is located in the Sudetes Mountains (southwestern Poland), near the city of Wroclaw. Dickite is found throughout the abandoned coal mine Piast near the town of Nowa Ruda.

Analysis and fractionation

The fractionation procedure was similar to that used by Premović [4]. The flow chart in Fig. 1 outlines the major steps in preparing the four fractions.

Inductively coupled plasma–optical emission spectroscopy (ICP–OES) analysis.

The Cr contents of the various fractions of dickite sample were analyzed by a Spectroflame ICP–OES instrument using Ar as the plasma gas.

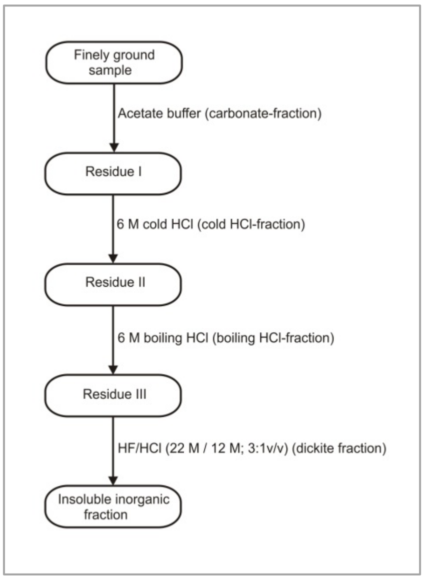

Fig.1. Flow chart of fractionation procedure.

Results and discussion

Table l shows the distributions of Cr among the fractions of dickite sample. These results show that most of Cr is containing in the dickite (>96 % of the total Cr (410 ppm)), indicating that the bulk of Cr resides primarily within the dickite structure.

Table 1. Geochemical distributions of Cr [ppm] from selective leaching experiments of dickite sample.

Fraction	Sediment (±5 wt%)	Cr
Acetate buffer	3	35
Cold-HCl	1	190
Boiling-HCl	3	340
Dickite	91	435
Insoluble residue	2	-
Total sample	100	410

Geochemical data suggest that the geological conditions under which dickite formed must have been relatively rich in Cr (i.e., Cr^{3+}), and it was introduced into dickite during formation aided by an invasive hydrothermal water. The fact that >96 % of Cr (Table l) resides within the dickite structure indicates that most Cr in dickite-forming solution was in a dissolved form.

We suggest that most of this metal was introduced into dickite by this solution already enriched in Cr.

The combination of geochemical and spectroscopic tools applied on Cr^{3+} allow one to specify the Eh (>0.4 V, highly oxidizing) and pH (≤4.0, highly acidic) of the solution during the formation of dickite from the Nowa Ruda Basin (Fig. 2).

Conclusion

1. The geochemical analysis of the dickite sample shows that the most of Cr is containing in the dickite fraction.
2. From the geochemistry of Cr^{3+}, it is deduced that the oxidation potential, Eh, and pH of the dickite-forming solution were >0.4 V and ≤4, respectively.

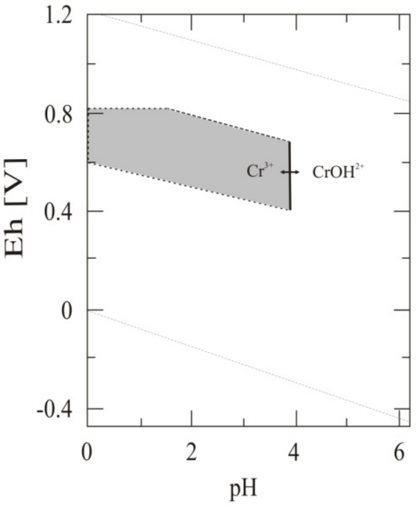

Fig.2. Eh-pH diagram for Cr^{3+} at 300 K and 1 atm for formation of dickite. The shaded area represents Eh/pH region of the hydrothermal waters defined by Kraynov and Ryzenko [5].

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