OXYGEN ISOTOPE STUDY OF CHROMIUM-BEARING KAOLINITE
AND DICKITE FROM TESLIĆ, YUGOSLAVIA

Key Words—Chromium, Dickite, Hydrothermal, Kaolinite, Oxygen isotopes.

Cr-bearing kaolinite and Cr-bearing dickite are exceptionally rare in nature. The enrichment of chromium in clays usually occurs as a result of hydrothermal alteration or weathering of ultramafic rocks where Cr^{3+} replaces Al^{3+} in the octahedral sites in the crystal structure. One of the well-known occurrences of Cr-bearing clays is located near the town of Teslić in Bosnia, Yugoslavia. In this locality, Cr-bearing clays form part of an argillic zone in hydrothermally altered ultramafic rocks. The 30-m thick zone is composed of a Cr-smectite subzone in the marginal part and a Cr-kaolinite subzone closer to a central quartz-pyrite vein. In general, the quartz content of the clay-quartz mixture increases closer to the quartz-pyrite vein. The mineralogical and chemical changes which followed the alteration process have been studied by Maksimović and Crnković (1968). Detailed X-ray powder diffraction, optical absorption, and infrared spectra studies revealed the presence of dickite together with a well-crystallized kaolinite (Maksimović *et al.*, 1981). These minerals usually are mixed in various proportions, but samples containing a single clay phase have also been found. The chromium content in the kaolinite and dickite averages about 0.6 wt. % (Maksimović *et al.*, 1981).

Although the kaolinite and dickite are known from field and petrological evidence to have formed by hydrothermal alteration, the specific conditions under which the alteration process occurred are not clear. Because oxygen isotope fractionation among coexisting mineral and fluid phases is a function of temperature at equilibrium, measurement of such data can provide a means of testing for equilibration among phases and a measure of the temperature of equilibration.

In this report, the results of oxygen isotope measurements on some of the Cr-bearing clays from Teslić are presented, including the three samples studied in detail by Maksimović *et al.* (1981). We are particularly interested in knowing whether the clays formed in isotopic equilibrium with the coexisting quartz, an unambiguous mineral intimately associated with the clays in the hydrothermal alteration zone, and if they were, what was the temperature of formation of the clays and the source of aqueous fluids responsible for the hydrothermal alteration of the parent ultramafic rocks.

EXPERIMENTAL

Most of the samples studied contain very fine-grained quartz intimately associated with kaolinite and dickite. Because it was not feasible to separate these phases, $^{18}O/^{16}O$ determinations were performed on the mixtures. The proportion of kaolinite and dickite was estimated by the X-ray powder diffraction (XRD) method (Brindley, 1980), using line intensity data and known mixtures of a well-crystallized kaolinite and dickite. The amount of quartz (and kaolinite) in the samples was determined by $Na_2S_2O_7$ fusion (Jackson, 1975). Anatase, detected by XRD in one sample, was determined by chemical analysis. In the samples studied, kaolinite and dickite were the only clay minerals detected.

Oxygen was extracted from the silicates using BrF_5 and was subsequently converted to CO_2. Isotopic analysis of water was performed by equilibration with CO_2 at 25°C; the fractionation factor, $\alpha_{CO_2-H_2O}$, was assumed to be 1.0412 (O'Neil *et al.*, 1975). The CO_2 was measured on an isotope-ratio mass spectrometer and is reported in δ-notation in per mil (‰) relative

to standard mean ocean water (SMOW). The analytical errors are about 0.1–0.2‰. A silicate reference sample NBS-28 was routinely included in the analysis and yielded an average δ-value of 9.6‰. The analytical results are shown in Table 1.

RESULTS AND DISCUSSION

Figure 1 shows a plot of $\delta^{18}O$ vs. clay content (kaolinite + dickite) for the 11 samples from the argillic alteration zone. The data points define an excellent mixing line ($r^2 = 0.98$) implying that each sample consists of a mixture of two end-members (i.e., clay and quartz) with a constant isotopic composition. The $\delta^{18}O$ values of the two end-members can be estimated by extrapolating the mixing line to 100% and 0% clay which yields:

$$\delta^{18}O \text{ clay} = 6.7‰, \delta^{18}O \text{ quartz} = 15.1‰.$$

Note that the latter value agrees precisely with that determined from analysis of pure quartz (sample 665-7). Also note that samples with dickite as the major phase in the clay fraction (samples 2378 and 664) fall on the same mixing line as those with kaolinite as the predominant phase implying that kaolinite and dickite have essentially the same isotopic composition in the samples studied. This similarity is to be expected because kaolinite and dickite have practically identical chemical compositions and crystal structures. Identical values of $^{18}O/^{16}O$ in kaolinite and dickite have been observed in a clay deposit at Tolfa, Italy, by Lombardi and Sheppard (1977).

The $\delta^{18}O$ value of 6.7‰ obtained for the kaolinite and dickite from this study falls within the range displayed by the hydrothermal kaolinites (Sheppard *et al.*, 1969; Taylor, 1974). It is definitely lower than values obtained from kaolinites of weathering and authigenic origin which generally fall between 15 and 23‰ (Savin and Epstein, 1970; Lawrence and Taylor, 1972; Shieh and Suter, 1979).

The observation that the kaolinite, dickite, and quartz in the alteration zone at Teslić have essentially the same isotopic composition suggests that isotopic equilibrium among the
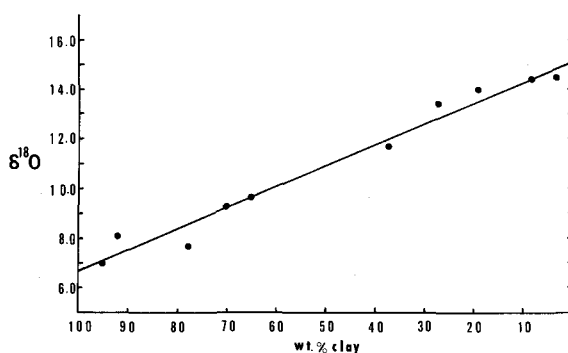

Figure 1.   Plot of $\delta^{18}O$ vs. clay content (kaolinite + dickite) in wt. % for samples from the argillic alteration zone. Line represents least squares fit ($r^2 = 0.98$) of data points which extrapolated to $\delta^{18}O = 6.7$ at 100% clay and $\delta^{18}O = 15.1$ at 0% clay.

318

Table 1. $^{18}O/^{16}O$ analyses of clay-quartz mixture and ground water from Yugoslavia.

Sample number	Kaolinite (%)	Dickite (%)	Quartz (%)	Anatase (%)	$\delta^{18}O‰$
Argillic alteration zone (Teslić)					
2378	10	85	5	—	7.0
665	82	10	6.4	1.6	8.1
665-1	78	—	22	—	7.7
664	35	35	30	—	9.3
665-2	65	—	35	—	9.6
6072	37	—	63	—	11.7
6073	27	—	73	—	13.4
6075	19	—	81	—	14.0
665-4	8	—	92	—	14.4
664-6	3	—	97	—	14.5
665-7	0	—	100	—	15.1
Weathering profile (Goleš Mountain)					
6069-Q (bottom)	0	—	100	—	25.0
6070-Q (top)	0	—	100	—	24.6
6820 (ground water)					−9.7

— = not detected.

three minerals was probably attained. The oxygen isotope fractionation between quartz and kaolinite can therefore be used to calculate the temperature of formation of the clays if isotopic fractionation between quartz and kaolinite (α_{q-k}) as a function of temperature is known. The oxygen isotope fractionation between quartz and water has been experimentally determined by Clayton *et al.* (1972) at 200°–500°C to be:

$$1000 \ln \alpha_{q-w} = 3.38(10^6/T^2) - 3.40.$$

Matsuhisa *et al.* (1979) redetermined the quartz-water curve between 250° and 500°C and obtained:

$$1000 \ln \alpha_{q-w} = 3.34(10^6/T^2) - 3.31.$$

The above equation is essentially identical to that of Clayton *et al.* (1972). The fractionation between kaolinite and water as a function of temperature is less certain. Kulla and Anderson (1978), based on partial isotope-exchange experiments between 172° and 319°C, obtained:

$$1000 \ln \alpha_{k-w} = 2.05(10^6/T^2) - 3.85.$$

Taylor (1974) gave an empirical fractionation curve, inferred from natural samples, which can be represented by the following equation:

$$1000 \ln \alpha_{k-w} = 2.53(10^6/T^2) - 4.90.$$

The kaolinite-water curve of Kulla and Anderson, when applied to kaolinites of authigenic and weathering origin, generally gives unreasonably low temperatures of less than 0°C (Shieh and Suter, 1979). We therefore believe that the Kulla-Anderson curve may not be completely valid when extrapolated to low temperatures. On the other hand, Taylor's curve, in most cases, gives more reasonable temperatures. If the quartz-water curve of Matsuhisa *et al.* (1979) is combined with the kaolinite-water curve of Taylor (1974), the following quartz-kaolinite oxygen isotope fractionation curve is obtained:

$$1000 \ln \alpha_{q-k} = 0.81(10^6/T^2) + 1.59.$$

When the above curve was applied to the argillic alteration zone at Teslić, the temperature of formation of the kaolinite and quartz was calculated to be 74°C, consistent with hydrothermal origin for the minerals. The $\delta^{18}O$ value of water responsible for the hydrothermal alteration is calculated to be −9.3‰. This value is essentially identical to that observed for local meteoric water at Goleš Mountain ($\delta^{18}O = -9.7‰$, sample 6820). It thus appears that meteoric water made up the bulk of the hydrothermal solution from which the Cr-kaolinite and Cr-dickite formed.

In addition to samples from Teslić, two secondary quartz samples from a well-studied weathering profile of ultramafic rocks from Goleš Mountain, Yugoslavia (Maksimović, 1973) were also analyzed and compared with those from the hydrothermal alteration zone. This weathering profile is in the same ultramafic belt, but about 300 km on the southeast of Teslić. The analyses gave $\delta^{18}O = 24.6$ and 25.0, respectively, for the top and bottom samples in the profile. These values are distinctly higher than the values measured for quartz samples from the hydrothermal alteration zone ($\delta = 15.1$). Assuming that the quartz formed in isotopic equilibrium with local meteoric water ($\delta^{18}O = -9.7‰$), the temperature of formation of the secondary quartz is 24°–26°C, in excellent agreement with their weathering origin.

In conclusion, despite the possible uncertainties in the oxygen isotope fractionation between mineral and water when extrapolated to low temperatures, oxygen isotope data obtained on the clay minerals and their coexisting phases give significant information on the origin and conditions of formation of the clays, particularly with regard to the temperature and source of the aqueous fluid. At Teslić, hydrothermal alteration of ultramafic rocks which produced Cr-bearing kaolinite and dickite occurred at a temperature of 70°–80°C. The hydrothermal solution causing the alteration was derived mainly from local meteoric waters.

Department of Geosciences   Yuch-Ning Shieh
Purdue University
West Lafayette, Indiana 47907

Faculty of Mining and Geology   Zoran Maksimović
University of Belgrade
11000 Belgrade, Yugoslavia

REFERENCES

Brindley, G. W. (1980) Quantitative X-ray mineral analysis of clays: Ch. 7, in *Crystal Structures of Clay Minerals and their X-ray Identification,* G. W. Brindley and G. Brown, eds., Mineralogical Society, London, p. 411.

Clayton, R. N., O'Neil, J. R., and Mayeda, T. (1972) Oxygen isotope exchange between quartz and water: *J. Geophys. Res.* **77,** 3057–3067.

Jackson, M. L. (1975) *Soil Chemical Analysis: Advanced Course:* 2nd ed., 10th printing. Published by the author, Madison, Wisconsin, p. 514.

Kulla, J. B. and Anderson, T. F. (1978) Experimental oxygen isotope fractionation between kaolinite and water: *U.S. Geol. Surv. Open-File Rept.* **78-701,** 234–235.

Lawrence, J. R. and Taylor, H. P., Jr. (1972) Hydrogen and oxygen isotope systematics in weathering profiles: *Geochim. Cosmochim. Acta* **36,** 1377–1393.

Lombardi, G. and Sheppard, S. M. F. (1977) Petrographic and isotopic studies of the altered acid volcanics of the Tolfa-Cerite area, Italy: the genesis of the clays: *Clay Miner.* **12,** 147–162.

Maksimović, Z. (1973) Nickel clay minerals in some laterites, bauxites and oolitic iron ores: in *6th Conference on Clay Mineralogy and Petrology, Czechoslovakia, 1971,* J. Konta, ed., 119–134.

Maksimović, Z. and Crnković, B. (1968) Halloysite and kaolinite formed through the alteration of ultramafic rocks: *Trans. Intern. Geol. Congress, Prague* **14,** 95–105.

Maksimović, Z., White, J. L., and Logar, M. (1981) Chromium-bearing dickite and chromium-bearing kaolinite from Teslić, Yugoslavia: *Clays & Clay Minerals* **29,** 213–218.

Matsuhisa, Y., Goldsmith, J. R., and Clayton, R. N. (1979) Oxygen isotopic fractionation in the system quartz-albite-anorthite-water: *Geochim. Cosmochim. Acta* **43,** 1131–1140.

O'Neil, J. R., Adami, L. H., and Epstein, S. (1975) Revised value for the ^{18}O fractionation between CO_2 and water at 25°C: *U.S. Geol. Surv. J. Research* **3,** 623–624.

Savin, S. M. and Epstein, S. (1970) The oxygen and hydrogen isotope geochemistry of clay minerals: *Geochim. Cosmochim. Acta* **34,** 25–42.

Sheppard, S. M. F., Nielsen, R. L., and Taylor, H. P. (1969) Oxygen and hydrogen isotope ratios of clay minerals from porphyry copper deposits: *Econ. Geol.* **64,** 755–777.

Shieh, Y. N. and Suter, T. G. (1979) Formation conditions of authigenic kaolinite and calcite in coals by stable isotope determinations: *Clays & Clay Minerals* **27,** 154–156.

Taylor, H. P., Jr. (1974) The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition: *Econ. Geol.* **69,** 843–883.