

Present day serpentinization in New Caledonia, Oman and Yugoslavia

IVAN BARNES and J. R. O'NEIL

U.S. Geological Survey, Menlo Park, CA 94025, U.S.A.

and

J. J. TRESCASES

Office de la Recherche Scientifique et Technique Outre-Mer, Paris, France

(Received 28 March 1977; accepted in revised form 25 August 1977)

Abstract—Geochemical evidence for modern low-temperature serpentinization has been found in three new localities. Apparently the low-temperature reactions are a common mode of formation of the lizardite–chrysotile and brucite assemblage. Possibly the ^{18}O content of serpentine formed at low temperatures is in part inherited from the pyroxene and olivine.

INTRODUCTION

GEOCHEMICAL evidence for low-temperature present-day serpentinization was first published by BARNES *et al.* (1967). A more thorough study by BARNES and O'NEIL (1971) showed that the $\text{Ca}^{2+}\text{-OH}^-$ -type waters associated with the areas investigated are supersaturated with respect to chrysotile, $\text{Mg}(\text{OH})_2$ end-member brucite, and diopside, and unsaturated with respect to forsterite and enstatite. BARNES *et al.* (1972) further showed these $\text{Ca}^{2+}\text{-OH}^-$ -type waters to be of meteoric origin. WENNER and TAYLOR (1971) also concluded that meteoric water reacts with ultramafic rocks to yield lizardite–chrysotile. Wenner and Taylor's temperature estimates of 85–115°C for the formation of lizardite–chrysotile and Barnes and O'Neil's inferred low temperature limit of mean annual temperature indicates a possible range of over 100°C for the formation of lizardite–chrysotile.

RESULTS

The results of chemical and isotopic analyses of spring waters from the United States, Oman, New Caledonia, and Yugoslavia are given in Table 1. The data for Yugoslavia are from DERKOVIC' (1973). The waters from the United States, Oman and Yugoslavia are similar in chemical composition. The compositions are apparently fixed by reactions between local meteoric waters and the ultramafic rocks because such chemical compositions are not reported for waters from any other type of rocks. The chemical compositions of the waters are independent of geographic location and, at least to some extent, climate. Mean annual precipitation ranges from 12.7 cm in Oman to 158 cm at Cazadero, Calif. On the other hand, the isotopic compositions of the waters are dependent on location and climate. As in many tropical areas bordering the sea, the Khafifah spring water from Oman is quite similar to seawater in

Table 1. Chemical and isotopic compositions of waters which have reacted to form serpentine. Concentrations in mg/l; $\delta^{18}\text{O}$ and δD are given in per mil relative to SMOW

	U.S.A.		OMAN Semail ophiolite		NEW CALEDONIA			YUGOSLAVIA	
	Cazadero, Calif.	Hahwalah, Wadi Jizi	Rustaq	Khafifah	La Coulée 1	La Coulée 2	Dumbea Riviere Bleue	Prony Ruisseau des Kaoris	Kulasi, Bosnia
pH	11.54	11.5	11.3	11.2	10.8	10.7	9.2	10.8	11.75
Temp. °C	20	25	28	28	23	23	23	34	29
Ca^{+2}	40	60	120	62	14.2	10.8	9	23	29
Mg^{+2}	0.3	0.1	0.2	0.2	2.3	5.9	---	---	7
Na^{+1}	19	230	110	110	14.6	26.1	7.7	12.8	35
K^{+1}	1.1	8	6.0	4.8	3	3.3	---	1.4	1.5
Cl^{-1}	63	280	170	140	22	16.3	8.5	30	20
SO_4^{-2}	0.4	9	5	3	0.75	5.8	---	---	---
HCO_3^{-1}	0	0	0	0	0	0	49	0	0
CO_3^{2-}	0	0	0	0	24	20	7.2	22	---
F ⁻¹	0	<0.1	<0.1	<0.1	---	---	---	---	0.34
Li^{+1}	---	0.01	0.02	0.03	---	---	---	---	0.06
NO_3^{-1}	0.1	---	---	---	---	---	---	---	0.05
SiO_2 (Total)	0.4	0.1	0.2	<0.1	0.4	2.8	1.2	3.7	1.9
B	0.02	<0.01	<0.1	---	---	---	---	---	0
$\delta^{18}\text{O}$	-6.45	-1.10	-1.69	+0.43	---	---	---	---	---
δD	-40.6	-5.1	-7.8	-0.6	---	---	---	---	---

O. R. S. T. O. M. 25 AVR. 1978

Collection de Référence

no 9131 geol. ex1

isotopic composition, but from the chemical composition it is of meteoric origin.

The $\delta^{18}\text{O}$ and δD values of a sample of chrysotile from the Semail ophiolite, Oman, are +7.84 and -65, respectively. If this serpentine were formed in waters similar in deuterium content to modern spring waters issuing from the Semail ultramafic body ($\delta\text{D} = -0.6$ to -7.8 , Table 1), the per mil fractionation of ~ -60 between serpentine and water would correspond to a formation temperature at 25°C or less (WENNER and TAYLOR, 1973; SUZUOKI and EPSTEIN, 1976). Thus the hydrogen isotope data support the concept of modern serpentinization in Oman by the action of ground water at low temperatures. However, oxygen isotope equilibrium does not obtain during the serpentinization process. Although the equilibrium ^{18}O relations between serpentine minerals and water have not been determined in the laboratory, we would expect from regularities in natural and experimental data that the serpentines would be at least 15‰ more enriched in ^{18}O than the water at the low temperatures suggested. Commonly chrysotile-serpentine from alpine-type serpentinites has δD values that suggest formation in meteoric waters and yet the $\delta^{18}\text{O}$ values will fall into the approximate range of 6-8‰ (WENNER, 1971), similar to the range found in normal ultramafic rocks. From isotopic analyses of serpentinizing fluids we know that, in general, the water-rock ratios in these systems are very high (BARNES and O'NEIL, 1971). If these present-day fluids are indeed similar to those that have produced the bulk of the chrysotile-lizardite serpentine, we are led to the intriguing possibility that chrysotile-lizardite can form with inheritance of intact silicate units from the precursor minerals olivine and pyroxene, thus preserving the ^{18}O composition of the original anhydrous ultramafic rock. Because the original ultramafic rocks are anhydrous, the hydrogen isotope composition can only be fixed by that of the reacting water.

The waters from New Caledonia have lower pH values, higher Mg^{2+} concentrations, and detectable CO_3^{2-} and HCO_3^- . The compositional differences between New Caledonia samples and those from the U.S.A. are not due to climate alone because mean annual precipitation of New Caledonia (109 cm) is within the range reported for samples analyzed in the U.S.A. The waters from New Caledonia are apparently intermediate in composition between the Mg^{2+} - HCO_3^- waters that result from the weathering of serpentinites (BARNES and O'NEIL, 1971) and the Ca^{2+} - OH^- waters whose compositions are fixed by the reaction of forsterite and enstatite to form brucite and lizardite-chrysotile serpentine. The components lost during serpentinization are CaO and NaCl. Although CaO is a pyroxene component, the source of the NaCl is not known.

SUMMARY AND CONCLUSION

Water compositions similar to those reported earlier for

low-temperature serpentinization reactions in Oregon and California have been found in New Caledonia, Oman, and Yugoslavia. Apparently the chemical relations reported by BARNES and O'NEIL (1971) are ubiquitous in serpentinization of primary ultramafic rocks at low temperatures. The chief chemical changes are hydration of the primary rocks and loss of the CaO component and, to some extent, a NaCl component. It is possible that the ^{18}O composition of lizardite-chrysotile is commonly inherited from the original anhydrous rocks with the D content being fixed by the reacting waters.

Acknowledgements—The samples from Oman were collected by E. H. BAILEY and R. G. COLEMAN of the U.S. Geological Survey and analyzed by T. S. PRESSER, also of the U.S. Geological Survey. Chemical and isotopic analyses were made with the help of T. S. PRESSER, L. H. ADAMI and L. D. WHITE.

REFERENCES

- BARNES I., LA MARCHE V. C., JR. and HIMMELBERG G. (1967) Geochemical evidence of present day serpentinization. *Science* **156**, 830-832.
- BARNES I. and O'NEIL J. R. (1971) The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, Western United States. *Bull. Geol. Soc. Am.* **80**, 1947-1960.
- BARNES I., RAPP J. B., O'NEIL J. R., SHEPPARD R. A. and GUDE A. J., III (1972) Metamorphic assemblages and the direction of flow of metamorphic fluids in four instances of serpentinization. *Contrib. Mineral. Petrol.* **35**, 263-276.
- DERKOVIC B. (1973) A new type of strongly hydroxide-sodium-calcium water at Kulasi (Bosnia) Yugoslavia. *Bull. Sci. Acad. Sci. Arts, Yugoslavia, Sect. A.*, v. 18, pp. 134-135.
- SUZUOKI T. and EPSTEIN S. (1976) Hydrogen isotope fractionation between OH-bearing minerals and water. *Geochim. Cosmochim. Acta* **40**, 1229-1240.
- WENNER D. B. (1971) Hydrogen and oxygen isotopic studies of serpentinization of ultramafic rocks. Ph.D. Thesis, California Inst. Technology, Pasadena, Calif.
- WENNER D. B. and TAYLOR H. P., JR. (1971) Temperatures of serpentinization of ultramafic rocks based on $^{18}\text{O}/^{16}\text{O}$ fractionation between coexisting serpentine and magnetite. *Contrib. Mineral. Petrol.* **32**, 165-185.
- WENNER D. B. and TAYLOR H. P., JR. (1973) Oxygen and hydrogen isotope studies of the serpentinization of ultramafic rocks in oceanic environments and continental ophiolite complexes. *Am. J. Sci.* **273**, 207-239.