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Stable-Isotope Study of Volcanogenic- and
Sedimentary-Manganese Deposits

by

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Abstract

As part of the program for the comprehensive study of volcanogenic- and sedimentary-manganese deposits, we have conducted stable-isotope analyses of manganiferous samples to (1) determine the H- and O-isotope systematics of manganese minerals and (2) improve our understanding of the origin and evolution of manganese deposits in order to better assess and evaluate their resource potential. Our methodology, analytical results, and preliminary interpretations are given here.

The $\delta^{18}\text{O}$ values of manganese-oxide minerals from stratiform deposits in Nevada and Arizona range from about +1 to $-9^{\circ}/\text{oo}$, the δD values of romanechite and nsutite from Arizona range from -87 to $-109^{\circ}/\text{oo}$, and are only slightly lower than those of most hydroxyl-bearing minerals of similar occurrence. The estimated oxygen-isotope fractionation factors between manganese oxide minerals and water are ~ 1.001 at 2°C , and ~ 0.995 at 120°C ; the estimated hydrogen-isotope fractionation factor is about 0.900 at 120°C .

The deposits from both Arizona (Artillery Mountains) and Nevada (Three Kids, Virgin River) seem to have formed under similar conditions; however, Nevada deposits have a slightly higher thermal history than the Arizona deposits. The average formation temperature of the deposits is about 120°C . The Ladd and Buckeye deposits of the Franciscan Complex in California formed at lower temperatures ($<100^{\circ}\text{C}$) in the presence of methane in a marine environment. The carbonate was derived from the oxidation of methane.

The Molango deposits (Sierra Madre Oriental, Mexico) probably formed on or close to the sea floor in organic-rich carbonate sediment within an anoxic basin. During early diagenesis rhodochrosite, kutnahorite, Mn-calcite, and Mn-chlorite formed, probably from recrystallization of the sediment and breakdown of the earlier-formed carbonate. Carbon-isotope values range from -15.5 to $+1.1$, suggesting that both biogenic carbonate and organic matter provided carbon for the manganese carbonates.

Introduction

Stable-isotope ratios of H, C, O, and S in minerals reflect conditions of formation including pH, $f\text{O}_2$, and temperature--and the nature of the mineralizing fluid. Isotopic compositions are also used as a tool for investigating the origin and evolution of ore deposits. We have been studying the stable-isotope composition of volcanogenic- and sedimentary-manganese deposits of the western Cordillera of the USA and other circum-Pacific areas. This progress report includes a catalog of isotopic data, our preliminary results, and a general discussion of isotope geochemistry of manganese minerals. Future reports will include more detailed discussions of individual deposits, additional isotopic data, and relevant background geochemical and geological information.

Samples

The mineral separates analyzed are from deposits in Nevada, Arizona, California, and Mexico (Table 1). For comparison, bulk samples of deep-sea ferromanganese nodules and crusts of known conditions of formation were also analyzed. Techniques are being developed to obtain samples of greater purity

from both the marine and onland environments.

Analytical Methods

The mass-spectrometric determinations of stable-isotope compositions of H, C, O, and S are made on H₂, CO₂, and SO₂ gases prepared from the mineral and rock samples. The procedures for preparation of the gases vary depending on the kind of gas and the nature of the sample.

For the preparation of H₂ gas, the sample is placed in a stainless steel boat along with a quartz reaction tube enclosing a platinum crucible. This assembly is placed in a glove box with P₂O₅ as a dessicant. The platinum crucible was preheated to ~1150°C under vacuum. After dehumidification of the glove box, the sample was heated to 110°C on a hot plate for 2 hours to ensure the removal of the absorbed H₂O. The sample was then charged into the platinum crucible, degassed under vacuum at 110°C for one hour, heated to ~1100°C for one hour to liberate H₂O, and reacted with U at 750°C to form H₂ (Bigeleisen et al., 1952).

The CO₂ for C- and O-isotope measurements of carbonate was produced by acidification with 100% H₃PO₄ at 25°C for a few hours (for calcite) to three days (for rhodochrosite) (McCrea, 1950; O'Neil and others, 1969).

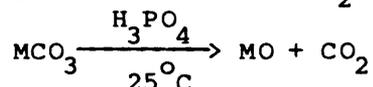
The CO₂ for O-isotope measurements of manganese minerals was prepared by a fluorination method (Taylor and Epstein, 1962). The prefluorination handling of the samples was modified from Yeh and Savin (1977). Samples were dried at 110°C in the glove box before being loaded into the nickel reaction vessels. After the reaction vessels were degassed for 2 hours under vacuum at 110°C, the samples were reacted with fluorine gas for 12 hours at 500°C. At the end of the fluorination, O₂ was separated from the other reaction products and the excess fluoride, and converted into CO₂ by red-hot graphite.

The SO₂ was prepared from pyrite by purification of the reaction products formed by heating a mixture of pyrite (~10 mg) and Cu₂O (50 mg) at 1000°C for 30 minutes. Separation of SO₂ from other gas products (i.e., CO₂, H₂O, and noble gases) was accomplished with liquid nitrogen, melt N-pentane, and dry ice as described by Robinson and Kusakabe (1975).

Isotopic Results

The isotopic results are given in Tables 1 and 2. All the results are reported in the δ-system, which is the deviation in isotopic ratios (i.e., D/H, ¹³C/¹²C, ¹⁸O/¹⁶O, and ³⁴S/³²S) of a sample from the standard in parts per thousand (‰) (O'Neil, 1979). The standards are SMOW (δD, δ¹⁸O), PDB (δ¹³C), and CDT (δ³⁴S) (Craig 1957, 1961; Thode and others, 1961).

The fractionation factor of 1.01025 was used for carbonate to obtain δ¹⁸O of carbonate oxygen from that of CO₂ generated according to:



where M stands for metal cation (i.e., Ca or Mn) (Sharma and Clayton, 1965). This may be slightly in error for Mn carbonates but will have no significant effect on the results (O'Neil and others, 1969).

The $\delta^{18}\text{O}$ values of a few untreated manganese-oxide samples may be slightly high because small amounts of silicate may be present. In general, however, errors resulting from contamination are insignificant and no correction is necessary.

Most of the results are averages of several analyses. The reproducibility of analyses varies for different types of samples and for different isotopes (Table 3). The poor crystallinity and the complexity of hydration in manganese nodules and crusts are the main causes of the poor reproducibility in these samples.

The δD values of pure romanechite (Table 1) are mostly in the range -101 to -109‰, but one sample has a value of -87‰. While the difference between these values is significantly large, the range of δD values for the more negative group is within the analytical uncertainty. The latter romanechite is a botryoidal vein sample. The δD value of sample 382-28-1A is -98‰; in addition to romanechite, the sample contains small amounts of cryptomelane and illite, without which the δD value would probably be more negative.

These δD values are within but toward the more negative end of the range of most hydroxyl minerals (Friedman and O'Neil, 1978), but are unlike the δD values of manganite reported by Hariya and Tsutsumi (1981). The δD values of the manganite studied by Hariya and Tsutsumi (1981) are -236 to -298‰. Thus, the hydrogen-isotope fractionation of romanechite is compatible with most hydroxyl minerals but is different from manganite.

The δD value of the pennantite from Molango, Mexico is -66‰ and is within the range for analyzed chlorites. The δD value of sample 782-29-2BII, which is a mixture of nsutite and pennantite, is -92‰. This indicates that nsutite is also within the range of most hydroxyl minerals regarding hydrogen-isotope fractionation.

The $\delta^{18}\text{O}$ values of all the manganese-oxide minerals range from +0.9 to -8.3‰ with most being between -6 to -8‰. The range of $\delta^{18}\text{O}$ values for Three Kids (Nevada) manganese oxide (+0.9 to -7.7‰) is virtually the same as that for the Artillery Mountains (+0.7 to -8.3‰). Hence, the manganese-oxide minerals are generally depleted in ^{18}O relative to other minerals, except perhaps iron oxides. The $\delta^{18}\text{O}$ value of the Molango pennantite is +13.9‰ which is common for chlorite. The $\delta^{18}\text{O}$ value of sample 782-29-2BII is +5.5‰, which contains, in addition to nsutite, about 30 percent pennantite and small amounts of quartz. The $\delta^{18}\text{O}$ values of both the quartz and the pennantite are most likely larger than +5.5‰; the $\delta^{18}\text{O}$ value of the nsutite is estimated to be about -1‰ and is thus within the range typical of the other Arizona-Nevada manganese oxides, +0.9 to -8.3‰. For comparison, the $\delta^{18}\text{O}$ value of an unspecified manganese oxide from the Blue Jay Mine in the Franciscan Complex, California, was estimated to be +1.5‰ (Chyi and others, 1984). The manganese oxides of the Three Kids Mine, Nevada are mainly pyrolusite with some todorokite, cryptomelane, and ramsdellite, whereas those of the Artillery Mountains, Arizona are principally romanechite with some cryptomelane, pyrolusite, and hollandite. It is evident that neither mineralogy nor geographic location of the manganese oxides is the principal control over the $\delta^{18}\text{O}$ values.

The $\delta^{13}\text{C}$ values of calcite from the Artillery Mountains are -1.6 and -2.4 ‰ and are indistinguishable from those of benthic foraminifera. This indicates that the main source of carbon in the calcite was the inorganic carbon dissolved in seawater and that the precursor carbonate was probably biogenic calcite. The $\delta^{13}\text{C}$ values of the Franciscan rhodochrosite range between -17.0 and -45.5 ‰ indicating that methane is the main source of carbon for the rhodochrosite. The $\delta^{13}\text{C}$ values for two Molango calcites are +0.7 and +1.1 ‰ and are within the range of those of planktonic foraminifera, indicating that the calcite was derived primarily from biogenic carbonate. The $\delta^{13}\text{C}$ values of Molango Mn-calcite (including kutnahorite) range from +0.2 to -15.4 ‰, indicating variable contribution of organic carbon to the carbonate carbon. The Molango rhodochrosites also show large variation in carbon-isotope compositions but generally are more depleted in ^{13}C (-3.7 to -15.5 ‰), indicating more contributions of CO_2 from bacterially degraded organic matter than in the Mn calcite.

The $\delta^{18}\text{O}$ values of two calcites from the Artillery Mountains are +15.2 and +15.3 ‰ and are about 8 to 13 ‰ lower than that of calcite precipitated from normal seawater (Savin and Yeh, 1981). A higher temperature of formation or the presence of meteoric water in the mineralizing fluid, or both, can bring about the lower $\delta^{18}\text{O}$ value; however, the $\delta^{13}\text{C}$ values of the calcite suggest that insignificant amounts of meteoric water were present.

The $\delta^{18}\text{O}$ values of two Molango calcites are +25.1 and +26.0 ‰. These are only slightly lower than those of calcite precipitated from a pre-glacial warm ocean and indicate that the Molango calcite may be largely primary. This conclusion is consistent with carbon-isotope data. The $\delta^{18}\text{O}$ values of Molango Mn calcites and kutnahorite are identical to those of Molango calcite and range from +25.2 to +26.2 ‰; these values indicate that these Mn carbonates also formed at low temperatures over a narrow range (1° to 2°C). The $\delta^{18}\text{O}$ values of Molango rhodochrosites range from +20.4 to +29.6 ‰; this large range of $\delta^{18}\text{O}$ values reflects a wide range of conditions of formation. The $\delta^{18}\text{O}$ values of Franciscan rhodochrosites range from +19.5 to +26 ‰, reflecting elevated temperature of formation or low $\delta^{18}\text{O}$ value of the mineralizing water, or both.

The $\delta^{34}\text{S}$ values of four Molango pyrite samples are within a narrow range from +2.4 to +3.8 ‰. Assuming that pyrite is the predominant sulfur mineral in the deposits, these $\delta^{34}\text{S}$ values indicate an igneous source for the sulfur.

H- and O-Isotope Geochemistry

The relations between H- and O-isotopic compositions of manganese minerals, the isotopic composition of the mineralizing fluid, and the temperature at which the mineral and the water establish isotopic equilibrium are little known. Increased knowledge of these relations would allow delineation of the environments of formation of manganese ores from isotopic compositions of the manganese minerals.

To investigate the relations experimentally, it is necessary to analyze the isotopic compositions of manganese minerals that have undergone isotope exchange with water of known isotopic composition within a range of known temperatures. Although our investigation of this subject has just started, a

few qualitative conclusions can be made and will be useful in the later discussions. These tentative conclusions are: (1) The oxygen-isotope fractionation factor between manganese dioxide and water at 2°C appears to be 1.001; (2) this factor changes to about 0.995 at 120°C. Conclusion (1) was derived from the isotopic results of manganese crusts and conclusion (2) from the results of sample 382-29-1DII (Table 1).

Discussion

Three Kids Mine, Clark County, Nevada

The three kids deposits consist of Neogene sandstone and siltstone with intercalated volcanic tuff and gypsum. Manganese oxides occur as cement in the terrigenous clastic rocks.

The 8.6 ‰ variation in $\delta^{18}\text{O}$ values of the Three Kids manganese minerals is mainly due to the variation in the $\delta^{18}\text{O}$ value of the mineralizing water and the variation in temperature of formation. Evaluation of the variation in $\delta^{18}\text{O}$ values of the manganese minerals will be made in the future by: (1) obtaining an isotopic geothermometer independent of the $\delta^{18}\text{O}$ value of the mineralizing water, (2) investigating the δD values of hydroxyl minerals and fluid inclusions, and (3) correlating $\delta^{18}\text{O}$ values with the lithology and mineral assemblage of the host rocks.

We do not have isotopic data of coexisting minerals yet, and thus, quantitative, independent temperatures of formation of the manganese minerals cannot be calculated. From the lithology and mineralogy of the deposits, we judge that formation temperatures of $120^\circ \pm 100^\circ\text{C}$ are reasonable. Assuming $120^\circ \pm 100^\circ\text{C}$ as the temperature of formation, the $\delta^{18}\text{O}$ value of the mineralizing water is estimated, with the fractionation factor derived above, to be between +4.1 and -2.7 ‰. This result indicates that the mineralizing water is predominantly seawater and that the deposits are of marine origin. Alternatively, the estimated formation temperatures vary from a few degrees centigrade to about 200°C under the assumption that the mineralizing water is normal seawater. Whether the deposits are hydrothermal or diagenetic cannot be determined yet, although the data favor a diagenetic model.

Artillery Mountains, Mohave County, Arizona

The Artillery Mountains deposits consist of Neogene sandstone and siltstone with interbedded felsic tuff. Manganese oxides occur as cement in the terrigenous clastic rocks.

The $\delta^{13}\text{C}$ values of the calcite, -1.6 and -2.4 ‰, indicate that neither magmatic nor meteoric water was involved in the formation of the deposits. The temperature of formation estimated from the $\delta^{18}\text{O}$ values of the calcite, assuming a $\delta^{18}\text{O}$ value of 0 ‰ for the mineralizing water, is $\sim 120^\circ\text{C}$ (O'Neil and others, 1969). The estimated $\delta^{18}\text{O}$ values of the mineralizing water range from +3.5 to -3.3 ‰. With a $\delta^{18}\text{O}$ value of 0 ‰ for the mineralizing water, the estimated formation temperatures of the manganese minerals range from a few degrees centigrade to about 200°C .

The δD value of the vein romanechite is about 14 ‰ higher than the average for stratiform romanechite. Assuming that the vein romanechite was formed from normal seawater, it is estimated that the percentage of meteoric water in the mineralizing water of the stratiform romanechite was about 10%.

As romanechite has the smallest $\delta^{18}\text{O}$ value, the 10% meteoric water is also the upper limit for the Artillery Mountain deposits in general.

The Artillery Mountain deposits may have undergone diagenetic readjustment. The Artillery Mountain deposits appear to have been slightly more affected by meteoric water or to have formed at a slightly lower temperature, or both, than the Three Kids deposits.

The origin of the mineralizing fluid, temperature of formation, and the history of formation derived from the isotope results are similar to the Three Kids deposits. The difference in mineralogy and chemistry between the two areas probably reflects the difference in the chemistry of the host rock rather than different modes of formation.

Franciscan Complex, Stanislaus and San Joaquin Counties, California

Manganese deposits occur as disc-shaped stratiform lenses within rhythmically-bedded chert-shale sequences of Late Jurassic age. The chert-shale sequences are interbedded with turbidity-current sandstone.

We analyzed six samples from the Ladd-Buckeye district. Five samples are composed of rhodochrosite, the other of nsutite and pennantite. One rhodochrosite sample (782-9-2BI) was obtained from the core of a hand-sample and the nsutite-pennantite (782-9-2BII) from the oxidation rim about 3-cm thick. We do not yet have the $\delta^{18}\text{O}$ values of separated pennantite and nsutite, and the carbonate-chlorite-manganese oxide isotope geothermometers may provide valuable information depending on the stage at which oxidation took place. If we assume again that the mineralizing water is normal seawater, the temperature of formation, estimated from the $\delta^{18}\text{O}$ values of the rhodochrosite, is $<100^\circ\text{C}$. The pennantite in isotopic equilibrium with seawater will have a $\delta^{18}\text{O}$ value of about $+10\text{‰}$ (Savin and Epstein, 1970; Wenner and Taylor, 1971). With this constraint, the estimated $\delta^{18}\text{O}$ value of the nsutite is about -1‰ . This result supports the contention that the Buckeye manganese deposit is of marine origin and formed at about 75°C . Similar conclusions can be derived from the hydrogen-isotope data.

The carbon-isotope composition of the rhodochrosite, $\delta^{13}\text{C}$ of -16 to -45.5 , requires that it formed by diagenesis during the oxidation of methane. Methane is the only natural carbon compound with $\delta^{13}\text{C} \leq -45.5\text{‰}$ (Deines, 1980).

Molango Deposits, Sierra Madre Oriental, Mexico

The Molango deposits consist of a sequence of organic-carbon-rich limestones and calcareous shales of Late Jurassic age. Manganese occurs as stratiform deposits in limestone with Mn-calcite, kutnahorite, and rhodochrosite as the primary manganese minerals.

The isotopic data clearly indicate that the Molango deposits formed during early diagenesis in an anoxic marine environment. The postulated igneous source of the pyrite sulfur requires removal of dissolved SO_4^{2-} in the interstitial waters and implies an anoxic environment where the SO_4^{2-} escaped from the pore waters as H_2S produced by bacterial reduction of seawater sulfate. The enrichment of ^{13}C in Mn-carbonates ($\delta^{13}\text{C} > -4\text{‰}$) indicates formation in a marine environment. Carbonates with the more negative $\delta^{13}\text{C}$

values formed from bacterially produced CO_2 , consistent with an anoxic marine environment.

The estimated formation temperatures are 17° to 67°C for rhodochrosite, 30° to 40°C for Mn calcite, and 30° to 38°C for calcite. The recrystallized calcites appear to have preserved their original carbon isotopic ratios ($\delta^{13}\text{C} = +0.7$ to $+1.1\text{‰}$). We can not determine the mechanism of the alteration from these data, but it must satisfy the constraint of recrystallization without the influence of bacterially produced CO_2 , at elevated temperatures.

All Mn calcite formed at an early stage of diagenesis as suggested by the isotopically determined temperature of 30° to 40°C . All Mn calcite (except 1182-17-3B) also contains some oxidized organic carbon, indicating the existence of organic-rich marine sediment. Sample 1182-17-3B ($\delta^{13}\text{C} = +1.1\text{‰}$) shows little evidence of oxidized organic carbon and probably formed at elevated temperature (30°C) in normal (in terms of the isotopic composition of the H_2O and the dissolved CO_2) seawater.

The rhodochrosites appear to form over a wide temperature range and invariably contain some oxidized organic carbon. The lowest estimated formation temperature, 17°C , is close to the seafloor temperature of the Jurassic (Savin, 1977) and is about 10°C lower than the lowest temperature estimated for calcite and Mn calcite formation. The highest estimated formation temperature of 67°C is about 30°C higher than the temperature for calcite and Mn calcite deposition. The low-temperature rhodochrosite apparently formed on or slightly below the seawater/sediment interface. Other rhodochrosites may have formed by recrystallization of the low-temperature rhodochrosite or earlier-formed Mn calcite during later diagenesis.

The isotopic data of the pennantite are consistent with formation at about 60°C , the temperature obtained from the $\delta^{18}\text{O}$ value of the coexisting rhodochrosite (1182-16-II). This low temperature indicates a diagenetic chlorite.

In summary, the Molango manganese deposit formed in an anoxic marine basin. The sediments were organic-carbon-rich biogenic carbonates. Initially, rhodochrosite formed as a replacement of biogenic carbonate on or slightly below the seawater/sediment interface; the lowest temperature of formation is 17°C , close to the Jurassic sea-floor temperature. Dissolution of pre-existing biogenic carbonate and bacterial sulfate reduction occurred at approximately the same time and provided the CO_3 for formation of rhodochrosite. About 35 percent of the rhodochrosite's CO_3 is organic carbon and about 65 percent inorganic carbon. The sulfate reduction probably went to completion and the H_2S escaped to the water column. During burial diagenesis, rhodochrosite recrystallized and some Mn calcite probably formed at that time. At a later stage of diagenesis, pennantite formed. These interpretations are tentative and subject to revision and refinement with the progress of our investigation.

Conclusions and Summary

(1) The δD values of nsutite, pennantite, and romanechite of marine hydrothermal or diagenetic origin are about -60 to -110 ‰ and are comparable to most other hydroxyl-bearing minerals of similar occurrence.

(2) The manganese-oxide minerals are highly depleted in ^{18}O relative to manganese silicate and carbonate and have compositions comparable to marine iron-oxide minerals.

(3) The estimated oxygen-isotope-fractionation factors for manganese-oxide minerals and water are 1.001 at 2°C, and 0.995 at about 120°C.

(4) The Three Kids deposits probably formed at a temperature near 120°C in the presence of seawater.

(5) The Artillery Mountains deposits probably formed under conditions similar to the Three Kids deposits. The mineralogical difference between the two may be the consequence of differences in the lithology of their host rocks.

(6) The Ladd-Buckeye deposits formed at about 75°C in the presence of seawater and methane.

(7) The Molango deposit originally formed on or close to the sea floor in an anoxic basin. Early diagenesis produced rhodochrosite and other manganese carbonates.

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Table 1. Isotopic composition of manganese minerals, pyrite, and calcite

Sample No.	Mineralogy	$\delta^{25}\text{Mn}$ (‰)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)	$\delta^{34}\text{S}_{\text{CDT}}$ (‰)	T*	Remarks
382-20-1G2	Cryptomelane			- 5.9		HF	Three Kids, Nevada
382-20-1H3	Todorokite			- 3.2		HF	Three Kids, Nevada
382-20-1J3	Pyrolusite			- 6.1		HF	Three Kids, Nevada
382-20-1N2	Pyrolusite + Todorokite			- 5.2		HF	Three Kids, Nevada
382-20-2D1	Pyrolusite			- 5.9		HF	Three Kids, Nevada
382-20-2E2	Pyrolusite + Todorokite			- 5.7		HF	Three Kids, Nevada
382-20-2H1	Pyrolusite (50%) + Todorokite (50)			- 2.3		HF	Three Kids, Nevada
382-20-2A1	Pyrolusite			- 2.3		HF	Three Kids, Nevada
382-20-2B2	Pyrolusite			- 6.2		HF	Three Kids, Nevada
382-22-1E1	Pyrolusite + Todorokite (Trace)			- 4.8		HF	Three Kids, Nevada
382-22-1G	Pyrolusite (92%) + Quartz			- 7.7		HF	Three Kids, Nevada
382-22-1G	Pyrolusite (92%) + Quartz			- 0.6		-	
382-23-1J1	Pyrolusite			+ 0.9		HF	Three Kids, Nevada
382-24-2A	Pyrolusite + (2%) Quartz			- 1.3		-	Virgin River Mine, Nevada
382-24-2R	Pyrolusite (85%) + Ramsdellite (15%)			- 0.3		-	Virgin River Mine, Nevada
382-28-1A	Romanechite + Cryptomelane + illite			+ 0.7		-	Maggie Mine, Lake Alamo, Arizona
382-28-7A2	Ramsdellite (50%) + Cryptomelane (50%)			- 7.0		HF	Artillery Mtns., Arizona
382-29-1C2	Romanechite			- 6.8		HF	Artillery Mtns., Arizona
382-29-1D1	Calcite		- 1.6	+15.3		HF	Artillery Mtns., Arizona
382-29-1DII	Calcite		- 2.4	+15.2		-	Artillery Mtns., Arizona
382-29-1DII	Romanechite			- 4.8		HCl	Artillery Mtns., Arizona
382-29-5C	Hollandite			+ 0.5		HF	Artillery Mtns., Arizona

Table 1 continued

Sample No.	Mineralogy	$\delta D_{SMOW} (‰)$	$\delta^{13}C_{PDB} (‰)$	$\delta^{18}O_{SMOW} (‰)$	$\delta^{34}S_{CDT} (‰)$	T*	Remarks
382-30-2G	Cryptomelane			- 0.3		HF	Artillery Mtns., Arizona
382-31-1A	Romanechite	- 105		- 8.3		-	American Mine, Lake Alamo, Arizona
482-1-2A	Pyrolusite (70%) + Cryptomelane + Romanechite			- 7.6		HF	Artillery Mtns., Arizona
482-3-1C	Romanechite	- 87		- 7.9		-	Chocolate Drop Mine, SE California
482-4-1Q	Romanechite	- 101		- 7.7		-	Yucca Mine, Lake Havasu, Arizona
482-5-3D	Romanechite	- 109		- 7.5		-	Black Jack Mine, SE California
782-29-2BI	Rhodochrosite		- 45.5	+ 19.5		-	Ladd-Buckeye District, Franciscan Complex, California
384-28-6A	Rhodocrosite		- 33.2	+ 26.6			Ladd-Buckeye District
484-20-2RII	Rhodochrosite		- 23.6	+ 21.6			Ladd-Buckeye District
484-20-2T	Rhodochrosite		- 16.6	+ 20.8			Ladd-Buckeye District
484-20-3A2	Rhodochrosite		- 29.2	+ 23.1			Ladd-Buckeye District
782-29-2BII	Nsutite (60%) + Pennantite (40%)	- 92		+ 5.5		-	Ladd-Buckeye District
283-9-3DI	Rhodochrosite		- 18.1	+ 22.2			Akatore Creek, S. Island of New Zealand
1182-16-2I-I	Rhodochrosite		- 13.4	+ 23.6		-	Molango District, Mexico
1182-16-2I-II	Rhodochrosite		- 12.7	+ 24.0		-	Molango District, Mexico
1182-16-2I-III	Pennantite			+ 13.9		HCl	Molango District, Mexico
1182-16-I	Pyrite	- 66			+ 3.4		
1182-16-2A	Rhodochrosite		- 9.1	+ 27.2		-	Molango District, Mexico
1182-16-2D	Kutnahorite		- 5.3	+ 25.6		-	Molango District, Mexico
1182-16-2E	Kutnahorite		- 2.5	+ 26.2		-	Molango District, Mexico
1182-16-2F	Calcite		+ 1.1	+ 26.2		-	Molango District, Mexico
1182-16-2G	Mn-Calcite		- 5.4	+ 24.7		-	Molango District, Mexico
1182-16-2G	Pyrite				+ 2.4	HCl	Molango District, Mexico
1181-16-2H	Calcite		+ 0.7	+ 25.1		-	Molango District, Mexico
1182-16-3A	Mn-Calcite		- 15.4	+ 26.4		-	Molango District, Mexico
1182-17-1	Kutnahorite		- 6.7	+ 25.8		-	Molango District, Mexico
1182-17-2BII	Rhodochrosite		- 3.7	+ 20.4		-	Molango District, Mexico
1182-17-2BII	Rhodochrosite		- 15.5	+ 22.0		-	Molango District, Mexico
1182-17-3B	Mn-Calcite		+ 0.2	+ 25.2		-	Molango District, Mexico

Table 1 continued

Sample No.	Mineralogy	$\delta^{18}\text{O}_{\text{SMOW}}(\text{‰})$	$\delta^{13}\text{C}_{\text{PDB}}(\text{‰})$	$\delta^{18}\text{O}_{\text{SMOW}}(\text{‰})$	$\delta^{34}\text{S}_{\text{CDT}}(\text{‰})$	T*	Remarks
1182-18-2A	Pyrite				+ 3.7	-	Molango District, Mexico
1182-18-2B	Pyrite				+ 3.8	-	Molango District, Mexico
1182-18-2C	Rhodochrosite		- 7.7	+29.6		-	Molango District, Mexico

*Indicates acid used to remove non-manganese minerals.

Table 2. Isotopic Composition of Ferromanganese Nodules and Crusts.

Sample No.	Manganese Phase	$\delta^{56}\text{Mn}_{\text{SMOW}} (\text{‰})$	$\delta^{55}\text{Mn}_{\text{SMOW}} (\text{‰})$	Remarks
N-A-1	Nodule	- 50	+ 6.1	Mid-Atlantic Ridge, Tag Site
N-P-1	Module	- 60	+11.2	N. Pacific, 20°N, 115°W, 4000m depth
N-F-1	Nodule	- 48	+ 3.5	Oneida Lake, New York
I5-82-SP-1-2	Crust, $\delta^{55}\text{MnO}_2$	- 70	+ 7.3	Tonga Platform
I5-82-SP-3	Crust, $\delta^{55}\text{MnO}_2$ + Todorokite	- 52	+ 6.4	Tonga Platform
Ye h-1a	Crust, Inner Part, $\delta^{55}\text{MnO}_2$	- 38	+11.3	Necker Ridge
Ye h-1B	Crust, Outer Part, $\delta^{55}\text{MnO}_2$	- 35	+14.1	Necker Ridge
Ye h-2a	Crust, Inner Part, $\delta^{55}\text{MnO}_2$	- 22	+13.4	Necker Ridge
Ye h-2b	Crust, Outer Part, $\delta^{55}\text{MnO}_2$	- 50	+11.9	Necker Ridge

(5)

Table 3. Standard Deviation ¹ of Isotopic Results

Sample	δD (‰)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	$\delta^{34}S$ (‰)
Manganese nodules and crusts	10		0.5	
Manganese minerals	3		0.3	
Carbonate		0.2	0.2	
Pyrite				0.2

1. Confidence level at better than 90% for the multiple analyses.