OXYGEN ISOTOPIC CONSTRAINTS ON THE ORIGIN OF NODULAR SILICA-APATITE FROM THE HAR PERES PYROCLASTICS, GOLAN HEIGHTS, ISRAEL

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Abstract—Oxygen isotope composition of three types of unique nodules which consist of amorphous silica-apatite, cristobalite-apatite and tridymite-apatite associations interspersed amidst basaltic pyroclastics from the Har Peres volcano, Golan Heights, Israel is reported. Unusual isotopic temperature (75°C) estimated from oxygen isotope fractionation between cristobalite ($\delta^{18}O$ = +25.5‰)-apatite ($\delta^{18}O$ = +12.9‰) pair suggests that the nodule was not formed by present-day pedogenesis as has been previously proposed, but was a xenolith incorporated probably from the underlying siliceous phosphorites at a higher temperature. An observed negative oxygen isotopic fractionation ($\delta^{18}O$ = −5.1‰) between tridymite ($\delta^{18}O$ = +9.9‰) and associated apatite ($\delta^{18}O$ = +15.0‰) is indicative of the nodular formation under disequilibrium conditions. A plausible mechanism of formation of the apatite (and calcite) associated with tridymite is an epitaxial overgrowth on template tridymite of magmatic origin under the current weathering regime. Oxygen isotopic evidence indicates a complicated origin for the nodules.

Key Words—Apatite, Har Peres pyroclastics, Oxygen isotope.

INTRODUCTION

Singer *et al* (1991) studied nodular minerals composed of silica-apatite which are interspersed amidst late Pleistocene basaltic pyroclastic strata in volcanic cones of the Golan Heights, Israel. The dominant mineral phase of silica is tridymite, with occasional amorphous silica, cristobalite and quartz. From field occurrence, solution chemistry of pore waters squeezed out from the pyroclastics and surface morphology as revealed by scanning electron microscopy, they proposed authigenic formation, where the minerals are precipitated from solutions draining pyroclastics that were undergoing meteoric weathering at normal temperature and pressure conditions.

The temperature dependence of oxygen isotope fractionations among silica-water and phosphate-water can be approximated by experimental, empirical and theoretical equations (Kyser 1987). The oxygen isotope fractionation between a co-existing mineral pair provides the equilibrium temperature of formation. Then the oxygen isotopic composition of ambient waters from which the minerals have precipitated can be estimated. Secondary modification due to oxygen isotopic exchanges with ambient waters under normal temperatures is limited as long as the original structure is retained (Juillet Leclerc and Labeyrie 1987; Shemesh *et al* 1988).

The objective of the present study is conducted to use oxygen isotope geothermometry to elucidate the genesis of the nodules consisting of silica-apatite association in pyroclastics from Golan Heights, Israel.

MATERIALS AND METHODS

Samples

The Golan Heights is a plateau of late Pliocene to late Pleistocene basalt at an elevation increasing from about 300 m in the south to 1000 m in the north. Whereas the older, southern part of the plateau is relatively flat and uneroded, the northern, younger part is characterized by several volcanic cones with recent pyroclastic materials (Singer *et al* 1991).

White clayey nodules are found within the pyroclastic strata (less than 0.1 m. y. old) of Har Peres volcano. Their size are in the range of 1 to 20 cm. Their shape is round in the vesicles, subangular when filling spaces between fragments. Chemical, X-ray diffraction and scanning electron microscopic studies have been reported by Singer *et al* (1991). Three specimens each containing a different polymorph of silica minerals (e.g., tridymite, cristobalite and amorphous silica) were selected for this study (Table 1). Euhedral tridymite, collected in a geode of andesite from Ishigami-yama, Kumamoto, Japan (Yamasaki 1937), was included as a reference of high temperature origin.

Analytical methods

One hundred to 200 mg of air-dry samples were digested with warm 10 M HNO_3 followed by filtration with a Millipore filter (pore size; 0.25 μm). A quantitative analysis of phosphorus in the extract suggested complete dissolution of apatite in samples. The silica residues were repeatedly washed with distilled water

Table 1. Oxygen and carbon isotopic ratios of silica/phosphate nodules from Har Peres volcano, Golan Heights, Israel.

Sample number	Major chemistry[1]					Silica polymorph	Isotopic composition			
							Oxygen (‰) SMOW			Carbon (‰) PDB
	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	P_2O_5 (%)	CO_2 (%)		Silica	Apatite	Carbonate	Carbonate
3	48.3	3.1	26.3	14.3	1.3	amorphous	+28.1	ND	ND	ND
4	59.2	2.0	19.6	12.4	1.4	cristobalite[2]	+25.6	+12.9	ND	ND
6	55.6	1.1	22.6	14.4	1.4	tridymite[2]	+9.9	+15.0	+24.7	−10.4

[1] Singer *et al* (1991) (Table 1).
[2] Contain trace of quartz (see Figure 1).
ND = not determined.

and dried to examine the mineral composition by powder X-ray diffraction analysis, using CoKα radiation. Phosphate in these extracts was collected and purified by standard chemical procedures (Tudge 1960) which involve precipitations first as phosphovanado-molybdate, then magnesium-ammonium phosphate and finally $BiPO_4 \cdot \frac{1}{2}H_2O$.

Oxygen was liberated from the silica minerals and $BiPO_4$ by a means similar to that described by Clayton and Mayeda (1963) and converted into CO_2. CO_2 was extracted from nodules in vacuum by reaction with 100% phosphoric acid at 25°C (McCrea 1950). These CO_2 products were analysed for their oxygen and carbon isotope compositions on one of two mass spectrometers (phosphate analysis with a VG 602E, and silica and carbonate analyses with a VG 903). The results are referred to the V-SMOW (Vienna standard mean ocean water) and PDB (Peedee Belemnite) oxygen and carbon-isotope standards and expressed in the conventional per mil notation (Craig 1961). Working standards were analysed in every manifold. Accuracy was established by analysing an international (NBS #28 quartz: $\delta^{18}O = +9.65‰$) and two laboratory standards (TSP phosphate: $\delta^{18}O = +15.1‰$, and CK-13 aragonite: $\delta^{18}O = +28.6‰$, $\delta^{13}C = +0.5‰$). Standard deviations are ± 0.1–$0.2‰$ for both of $\delta^{18}O$ and $\delta^{13}C$ from multiple runs.

RESULTS AND DISCUSSION

X-ray diffractometry

Figure 1 shows X-ray diffraction patterns of three insoluble residues from 10 M HNO_3 digestion. Sample number 3 gave no distinctive diffraction peaks, whereas sample numbers 4 and 6 showed dominance of crystalline silica. Strong and sharp diffraction peaks from cristobalite (sample number 4) and tridymite (sample number 6) indicate high crystallinity of these silica minerals. Peaks from other than the silica minerals were not detected on the diffractograms.

Oxygen isotope geothermometry

Oxygen yields of the silica separates were manometrically estimated during the preparation of CO_2 for mass spectrometry. High yields (amorphous silica: 99%,

cristobalite: 96%, tridymite: 96%) relative to theoretical oxygen content of the silica separates prove valid purity for isotopic analysis.

The oxygen isotopic composition of three silica specimens separated from the nodules ranged from +9.9 to +28.1‰ (Table 1). The isotopic composition is lowest in the sample composed of well-ordered tridymite (Figure 1) ($\delta^{18}O = +9.9‰$), but higher in the sample composed of amorphous silica ($\delta^{18}O = +28.1‰$) and cristobalite ($\delta^{18}O = +25.6‰$). Variable oxygen isotopic composition of the silica minerals indicates a diverse origin for the nodules. The oxygen isotope composition of tridymite separate ($\delta^{18}O = +9.9‰$) is distinctly higher than that of a specimen with typical volcanic origin from Ishigami-yama, Kumamoto, Japan ($\delta^{18}O = +5.5‰$), but seems still to be in ranges of primary magmatic and/or secondary hydrothermal origins (Garlick 1969). On the contrary, lower temperature origins of the amorphous silica (sample number 3) and cristobalite (sample number 4) were inferred from relatively higher isotopic ratios ($\delta^{18}O = +25.6$ to $+28.1‰$).

Oxygen isotope composition of two apatites separated from the nodules showed a little variation in range of +12.9 to +15.0‰. The isotopic compositions are distinctly higher than those of two volcanic apatites ($\delta^{18}O = +5.3$ and $+6.2‰$, Mizota *et al* 1992). Fairly high oxygen isotopic ratios of these two apatites ($\delta^{18}O = +12.9$ and $+15.0‰$), associated amorphous silica ($\delta^{18}O = +28.1‰$) and cristobalite ($\delta^{18}O = +25.6‰$) in the nodules are indicative of non-magmatic origins.

Calcite disseminated in sample number 6 showed oxygen and carbon isotopic ratios of +24.7 and −10.4‰ respectively. The oxygen isotopic ratio is distinctive from juvenile carbon ($\delta^{18}O = -7‰$) (Hoefs 1980). $\delta^{13}C$ and $\delta^{18}O$ values of the calcite is similar to reported for modern soil carbonates from Israel ($\delta^{13}C = -8.5 \pm 0.5$, $\delta^{18}O = +25.6 \pm 0.8‰$, Margaritz *et al* 1981).

If the silica, apatite and calcite in the nodules are formed authigenically from the percolating meteoric waters as proposed by Singer *et al* (1991), the resulting oxygen isotopic compositions of silica, phosphate and calcite can be calculated from oxygen isotope fractionation factors between mineral and water at ambient temperatures. The equations hitherto established are:
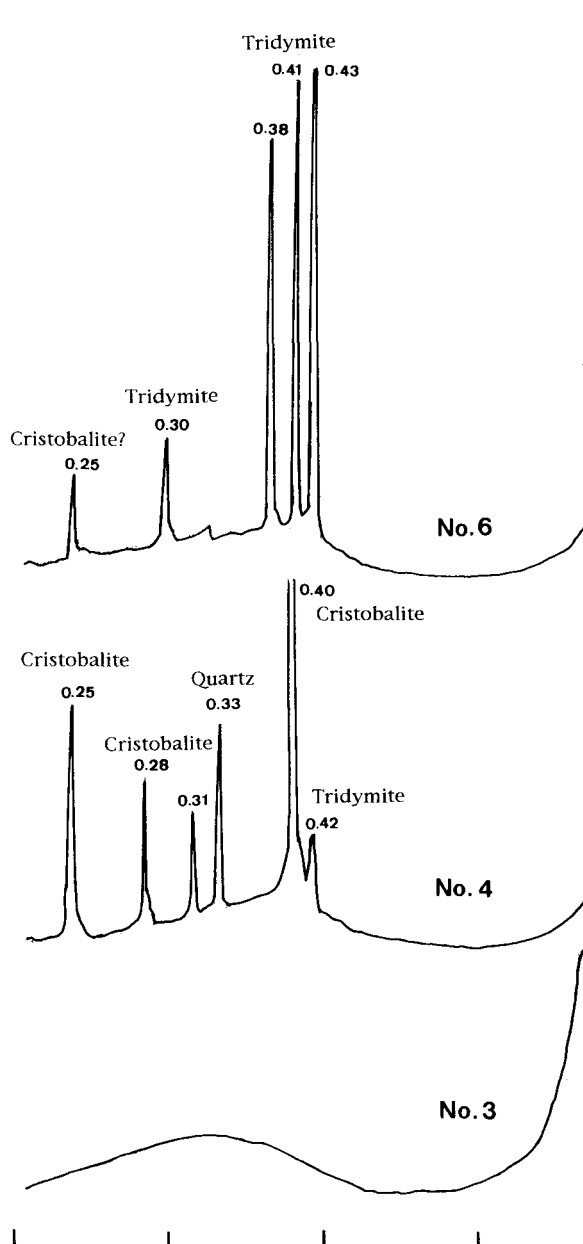
Figure 1. X-ray diffraction patterns of residues from 10 M HNO_3 digestion, using $CoK\alpha$ radiation. Small numbers in the figure indicate diffraction peaks in nm unit. Sample numbers correspond to those of Table 1. Positions of the major peaks corresponding to the silica minerals are given.

$$1000 \ln \alpha_{(silica-water)} = 3.26(10^6/T^2) + 0.45$$
(Juillet and Labeyrie 1987)

$$1000 \ln \alpha_{(phosphate-water)} = 2.12(10^6/T^2) - 2.98$$
(Shemesh *et al* 1988)

$$1000 \ln \alpha_{(calcite-water)} = 2.78(10^6/T^2) - 2.89$$
(Friedman and O'Neil 1977)

where T is an absolute temperature in Kelvin. Mean annual soil temperature (8–15°C: Dan and Singer 1973) and oxygen isotopic composition of local meteoric waters (−6 to −8‰: Gat and Dansgaard 1972) from nearby sample sites of the nodules are documented. The calculated oxygen isotope compositions of +32–+36‰, +15–+18‰, and +22–+26‰ for silica, apatite and calcite respectively are generally higher than measured values (Table 1), except for apatite ($\delta^{18}O = +15.0‰$) and calcite ($\delta^{18}O = +24.7‰$) in sample number 6. The results suggest that silica/phosphate nodule of sample numbers 3 and 4 are not crystallized from draining meteoric waters under present-day temperature regimes, as proposed by Singer *et al* (1991).

Close association of silica with apatite in the nodules has been shown by scanning electron microscopic observation (Singer *et al* 1991). If the minerals have precipitated from a solution at the same temperature, the oxygen isotopic fractionation factor between co-existing minerals can be employed. Subtracting phosphate-water equation (Shemesh *et al* 1988) from silica-water equation (Juillet Leclerc and Labeyrie 1987), we obtain the resulting equation which is a paleotemperature equation in $\delta^{18}O_{silica}$-$\delta^{18}O_{phosphate}$ space, independent of $\delta^{18}O_{water}$:

$$1000 \ln \alpha_{(silica-phosphate)} = 1.14(10^6/T^2) + 3.34$$

The equilibrium temperature and oxygen isotopic composition of pore waters estimated for cristobalite and apatite pair in sample number 4 is 75°C and −1.6‰ respectively. The calculated isotopic temperature and composition of equilibrium water are unrealistic relative to current conditions of surficial weathering of sampling areas (Dan and Singer 1973). In addition negative value (−5.1‰) of oxygen isotope fractionation between tridymite ($\delta^{18}O = +9.9‰$) and associated apatite ($\delta^{18}O = +15.0‰$) in sample number 6 indicates formation of the minerals under disequilibrium conditions.

From this, it can be concluded that the cristobalite and associated apatite in nodule (No. 4) were formed under higher temperature regimes than those normally encountered in the present-day environments. The estimated conditions of the formation are comparable to diagenetic conditions in sedimentary basins.

Basement rocks underlying the Har Peres pyroclastics are not observed in an outcrop from which the sample nodules are collected (Lang *et al* 1979; Singer *et al* 1991). Sedimentary rocks (chalk) of Eocene age overlying a series of basalt flows are identified in a deeply incised canyon-like valleys of Nahal Orvim in the northwestern Golan Heights (Singer and Ben-Dor 1987). Siliceous phosphorites alternating with chalk widely occur in the underlying Cretaceous to Eocene strata of the areas along Jordan Rift Valley (Shemesh and Kolodny 1988; Vengosh *et al* 1987). It is conceiv-

able that these deposits would be brought to near surface by volcanic eruption of the Har Peres volcano.

In contrast, tridymite in nodule (No. 6) is presumably of magmatic origin. In addition the mineral has not been identified as a primary constituent of the basic pyroclastic deposits (Lang *et al* 1979; Singer *et al* 1991). The most plausible mechanism for apatite and calcite crystallizations in the nodule (sample number 6) is a secondary overgrowth on the template of tridymite crystallites as proposed by Singer *et al* (1991). Whether major sources of phosphate and carbonate in the sample derive from the dissolution of pre-existing sedimentary deposits entrapted during the magmatic activity is not known from available data of field occurrence and oxygen isotope composition.

Clay-sized silica and phosphate minerals are ubiquitous in soils and sediments. Nodular forms of these minerals such as in case of this study are rather limited. The oxygen isotopic implications from the present study is a further potential use of the stable isotope signature by which conventional techniques can not provide direct evidence for clay mineral genesis.

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