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Synthesis, Ion-Exchange Behavior, and Analytical Applications of a New, Crystalline, and Stable Zirconium(IV) Arsenosilicate Cation-Exchanger: Analysis of Some Silicate Rocks

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Abstract

A new crystalline inorganic ion-exchanger, Zr(IV) arsenosilicate, has been synthesized and shows high chemical and thermal stability. It is also stable under γ-radiations of moderately high strength. The utility of this material has been demonstrated by achieving quantitative separation of Hg(II) from such other metal ions as Cd(II), Pb(II), Ni(II), Co(II), Zn(II), Al(III), and Fe(III) on its columns. Some silicate rocks have also been analyzed using this material.

INTRODUCTION

Silicates and phosphosilicates are generally more stable ion-exchangers both chemically and thermally than other materials of this class (*1–6*). Similarly, arsenates show good ion-exchange capacity and reproducibility in properties (*7–10*). An ion-exchange study of arsenosilicates of tetravalent metals is, however, lacking. Our present efforts are therefore to explore the possibility of preparing different arsenosilicates showing promising ion-exchange behavior and which are stable under high doses of γ-radiations. This article summarizes such a study for the synthesis of a crystalline Zr(IV) arsenosilicate capable of separating Hg(II) from other polluting metal ions. The actual application of the material has been demonstrated in the analysis of some rocks.

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EXPERIMENTAL

Reagents

The zirconyl chloride used in this study was a B.D.H. (England) product while the sodium silicate was a Riedel (Dehaenag, Seelze, Hanover) product. All other reagents and chemicals were of AnalaR grade.

Standard Rocks Used

The following rocks obtained (*11*) from the U.S.G.S. (U.S.A.) were analyzed: Andesite (AGV-1), Basalt (BCR-1 and BHVO-1), Granite (G-2), and Periodolite (PCC-1).

Apparatus

pH measurements were made on an Elico (India) Model LI-10 pH meter while IR studies were performed on a Beckman IR-20 spectrophotometer using KBr pellets. X-ray studies were made on a Philips x-ray unit with a Mo-K_α target. Colorimetry was done on a Bausch & Lomb spectronic-20 colorimeter. For thermogravimetric analysis a Modern TGA balance of the Fertilizers Corp. of India Ltd. was used, and for radioisotopic studies a well-type single channel analyzer with a NaI(Tl) detector, obtained from Ecil (India) was used. A Pye Unicam model SP 2900 atomic absorption spectrophotometer was used for the determination of elements in trace amounts.

Preparation of Ion-Exchange Materials

A large number of samples was prepared by varying the concentration and mixing volumes of the various components. However, the sample prepared in the following manner showed high ion-exchange capacity, chemical stability, and reproducibility in properties. An aqueous (0.1 *M*) sodium silicate solution, made acidic (pH 0–1) by adding HCl, was mixed with an aqueous (0.1 *M*) zirconyl chloride solution and the pH of the mixture was raised to 8–10 by the slow addition of ammonium hydroxide with intermittent shaking to obtain a slurry. After filtering and washing with demineralized water (DMW), it was treated with a 1:1 (v/v) mixture of 0.5 *M* solutions of arsenic and nitric acids. This resulted in a gel which was digested at room temperature for 24 h and then filtered out. It was washed thoroughly to remove excess acid, dried at 45°C, and cracked into small granules by putting in DMW. These were then sieved to obtain 60–100 mesh particles which were converted into the H^+-form using 1 M HNO_3. They were finally washed with DMW and dried as usual for further study.

Ion-Exchange Capacity (i.e.c.)

This was determined by the column process using 1 M $NaNO_3$ as the eluant and keeping a very slow flow rate (10–12 drops/min) of the effluent. The Na^+-ion exchange capacity of the material was found to be 1.3 meq/dry g.

Thermal Stability

Several 1 g portions of the sample were heated at various temperatures in a muffle furnace for 1 h each and their i.e.c.s were determined as usual after cooling them to the room temperature. The results are summarized in Table 1.

Chemical Stability

250 mg portions of the sample were kept with 25 mL each of the various solvents for 24 h at room temperature with intermittent shaking. The supernatent liquid was then analyzed for the presence of zirconium(IV),

TABLE 1

I.e.c. and General Appearance of ZAS after Heating to Various Temperatures

Heating temperature (°C)	I.e.c. (meq/dry g)	% Retention in i.e.c.	General appearance
45	1.30	100	Dirty white
100	1.30	100	Dirty white
200	1.25	96.2	Dirty white
400	0.46	35.4	White
600	0.20	7.7	White

arsenic(V), and silica using standard colorimetric methods (*12–14*). The results show the negligible amounts of them in the supernatent liquid even on using up to 4*M* acids such as HNO_3, H_2SO_4, HCl, $HClO_4$, and CH_3COOH and 0.1 *M alkali solutions such as NaOH and KOH.*

Composition

100 mg of the powdered sample was dissolved in a minimum amount of H_2SO_4 (conc.). The solution was then diluted to 100 mL with water and the amounts of zirconium(IV), arsenic(V), and silica were determined by standard gravimetric or titrimetric methods (*15–17*). The molar composition of the material was found to be 1:2:1 for Zr:As:Si.

pH Titrations

500 mg of the exchanger was taken in each of several 250 mL conical flasks followed by equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 mL to maintain the ionic strength constant. The pH of the solution was recorded after keeping it for 24 h to attain equilibration, and the pH was plotted against the milliequivalents of the OH^- ions added. Figure 1 shows the pH titration curves for the sample dried at 45°C using different alkalies and their respective chlorides as titrants, while Fig. 2 shows the variation of pH titration curves on heating and irradiating the sample.

TGA, IR, and X-Ray Studies

Figure 3 shows the percent weight loss that occurred in the sample on heating up to 700°C, and Fig. 4 shows the IR spectra of ZAS dried at room temperature and heated at 200°C. X-ray diffraction patterns reveal its crystalline nature and a *d*-value of 2.05 Å.

Distribution Studies

250 mg of the exchanger beads in the H^+ form was equilibrated with 25 mL of the selected solvent, either by shaking for 3–4 h or by keeping at room temperature for 24 h. The initial metal concentration in the solution was adjusted so that it did not exceed 3% of the total i.e.c. of the material. The

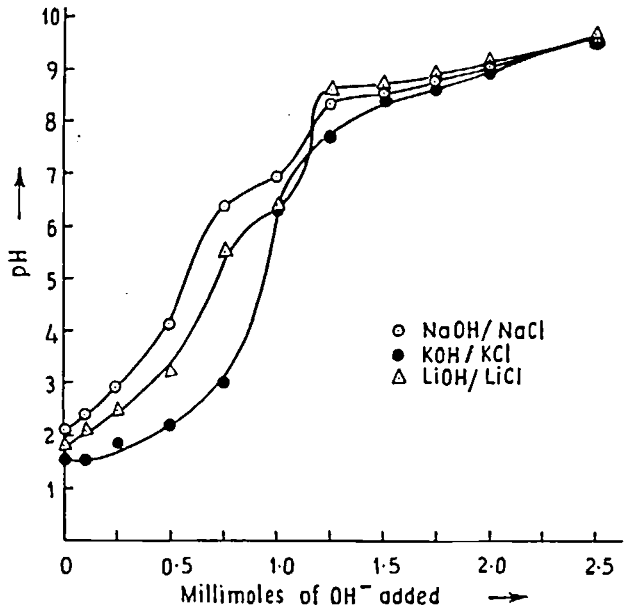

FIG. 1. pH titration curves for ZAS dried at 45°C using different alkalies and their chlorides as titrants.

determinations were carried out volumetrically using EDTA as the titrant (*18*). For alkali metals the tracer technique was used by employing the following isotopes (half-life periods in parentheses): ^{24}Na (15 h), ^{42}K (12.5 h), ^{86}Rb (18 d), ^{137}Cs (30.2 years).

The K_d values, as summarized in Table 2, were obtained by the equation

$$K_d = \frac{I - F}{F} \times \frac{V}{A} (\text{mL/g})$$

where I = initial amount of the metal ion in the solution phase
F = final amount of the metal ion in the solution phase
V = volume of the solution (mL)
A = amount of the exchanger (g)

The variation of K_d values of alkali metals with pH (fixed with HClO$_4$) is shown in the log K_d vs pH curves of Fig. 5.

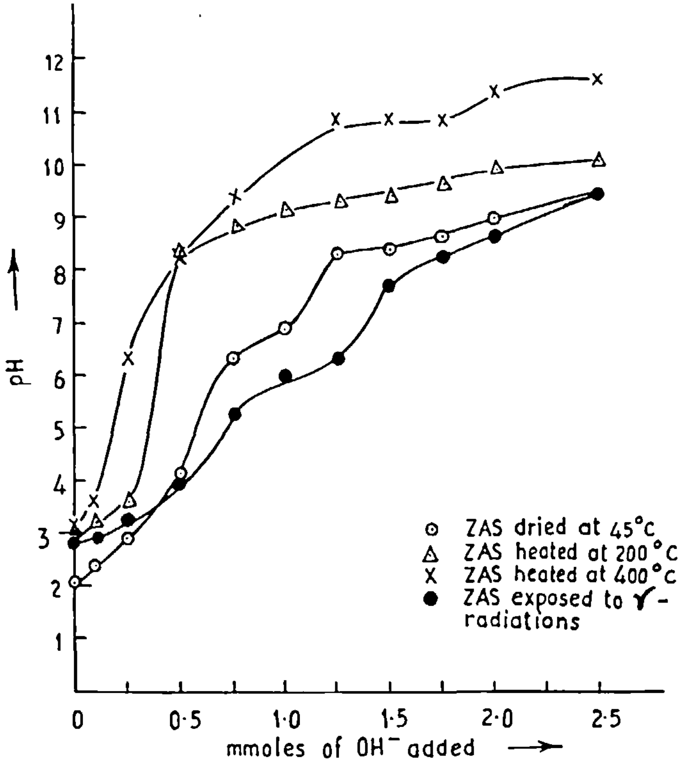

FIG. 2. pH titration curves for ZAS heated at different temperatures and for the irradiated sample using NaOH/NaCl as a titrant.

Separations Achieved

In Synthetic Mixtures

The 60–100 mesh sized particles of the exchanger (2 g) in the H^+ form were used for the column operation in a glass tube having an internal diameter of ~0.6 cm. The column was washed thoroughly with DMW and the mixture to be separated was loaded on it, maintaining a flow rate of ~2–3 drops/min. The separation was achieved by passing a suitable solvent through the column as eluant. The metal ions in the effluent were determined quantitatively by EDTA titration. The salient features of the separation of Hg(II) from other metal ions on ZAS columns are summarized in Table 3. A

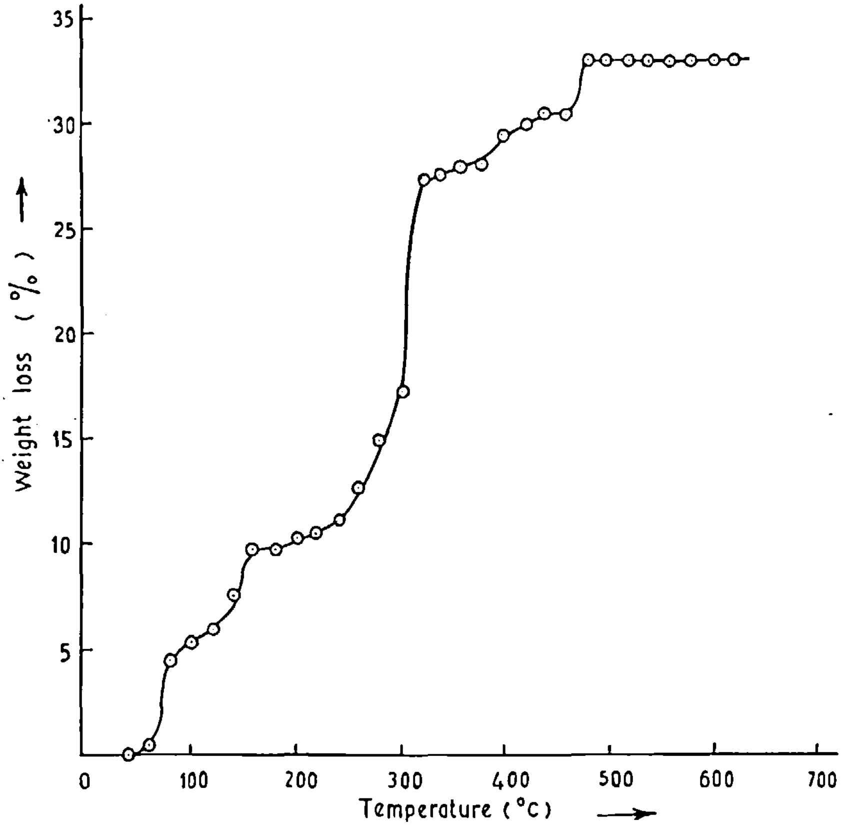

FIG. 3. TGA curve for ZAS in the H^+ form

synthetic mixture was also prepared containing 500 μg Hg(II) with other metal ions such as Cd (280 μg), Pb (520 μg), Zn (160 μg), Ni (180 μg), Co (147.25 μg), and Al (67.5 μg). Hg(II) was quantitatively recovered from this mixture using DMW as the eluant.

In Actual Rock Samples

For preparing standard rock solution, 100 mg of the sample was fused with NaOH in a Ni crucible at dull red heat followed by dissolution of the melt and dilution to a liter with dilute HCl. The analysis was performed as

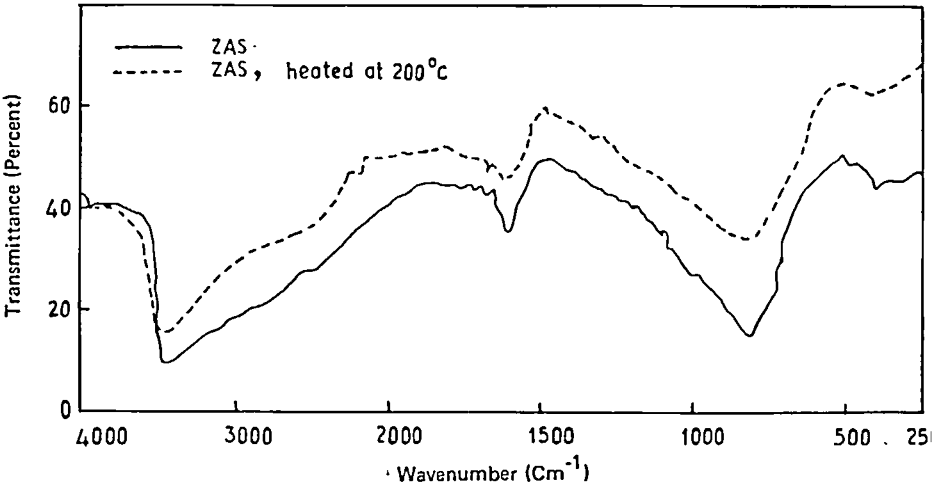

FIG. 4. IR spectra of ZAS dried at 45°C and at 200°C.

follows: 0.5 to 1 mL of the stock solution was evaporated to dryness to remove the excess acids. The residue was taken in DMW (~2 mL) and the solution was applied on the exchanger column (~2 g) as usual. All the elements except Fe and Al were eluted out with DMW. Al and Fe were recovered from the column with 1 *M* HNO_3 as the eluant. The quantitative determination of the elements was done by atomic absorption spectrophotometry. Table 4 summarizes the results.

Irradiation Effect

For such a study the sample was exposed to γ-radiations produced from a ^{50}Co source for 96 h with a dose rate of 0.4 Mrd/h using $FeSO_4$ as a dosimatter. The material was then observed for some of its physical and ion-exchange properties such as appearance, color, grain size, brittleness, i.e.c., elution behavior, K_d values, and pH titration. No change was reported in any of the above properties except the last one which is affected very slightly (Fig. 2).

DISCUSSION

The material obtained in these studies, Zr(IV) arsenosilicate, shows a cation-exchange capacity comparable with other materials of this class. It

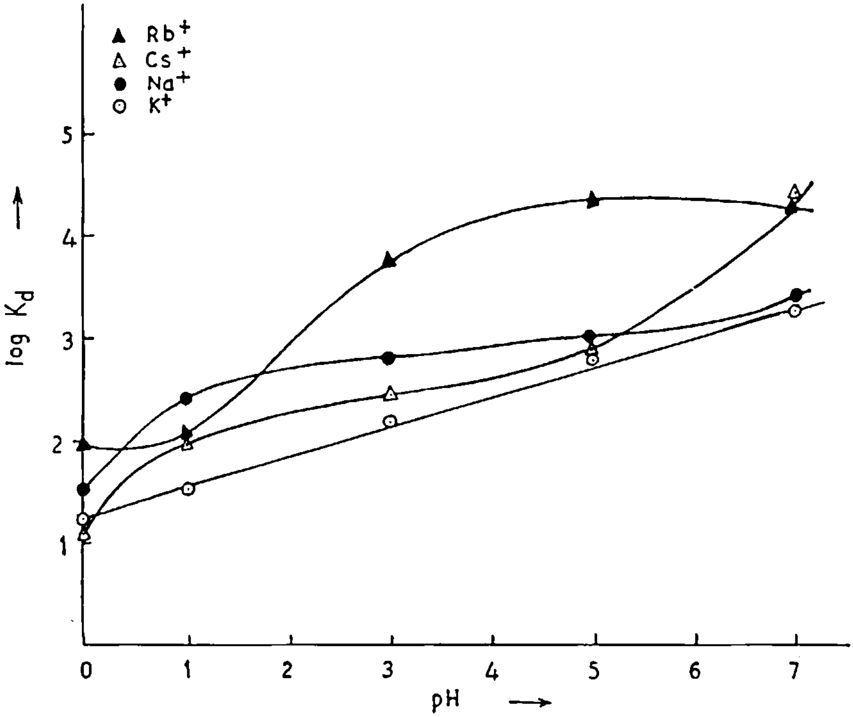

FIG. 5. Effect of pH on the K_d values of alkali metals on ZAS.

TABLE 2

K_d Values of Some Common metal Ions in Different Media for ZAS

Metal ions	DMW $(X \times 10^{-2})$	0.01 M HNO_3 $(X \times 10^{-2})$	0.1 M HNO_3 $(X \times 10^{-2})$	0.01 M $HClO_4$ $(X \times 10^{-2})$	0.1 M $HClO_4$ $(X \times 10^{-2})$
Ba(II)	1.10	1.05	0.91	3.00	1.63
Cd(II)	80.3	1.86	1.30	2.13	1.40
Pb(II)	54.3	15.8	14.6	54.3	54.3
Mg(II)	3.67	0.77	0.63	0.46	0.37
Sr(II)	2.18	0.35	0.03	0.41	0.13
Hg(II)	0.52	0.58	0.41	0.75	0.52
Mn(II)	0.69	0.13	0.09	0.20	0.13
Ca(II)	3.14	0.81	0.36	0.74	0.23
Zn(II)	10.0	0.57	0.36	0.57	0.26
Ni(II)	80.0	2.06	1.90	1.78	1.10
Co(II)	6.00	7.00	4.09	4.33	2.50
Al(III)	43.5	38.8	3.20	7.09	3.50
Fe(III)	38.5	2.93	2.10	1.26	0.97

TABLE 3

Some Binary Separations Involving Hg(II) on ZAS Columns

No.	Separations achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluant used	Volume of the eluant used (mL)
1	Hg(II)-Cd(II)	500 Hg	500 Hg	0	DMW	40
		280 Cd	280 Cd	0	0.1 *M* HNO_3	50
2	Hg(II)-Pb(II)	500 Hg	487 Hg	−2.6	DMW	
		520 Pb	520 Pb	0	0.1 *M* HNO_3 + 1 *M* NH_4NO_3	90
3	Hg(II)-Zn(II)	500 Hg	500 Hg	0	DMW	
		160 Zn	157 Zn	−1.9	0.1 *M* HNO_3	40
4	Hg(II)-Ni(II)	500 Hg	500 Hg	0	DMW	30
		180 Ni	179 Ni	−0.6	0.1 *M* HNO_3	70
5	Hg(II)-Co(II)	500 Hg	500 Hg	0	DMW	40
		147.25 Co	142 Co	−3.5	0.1 *M* HNO_3 + 1 *M* NH_4NO_3	50
6	Hg(II)-Al(III)	500 Hg	500 Hg	0	DMW	30
		67.5 Al	67.5 Al	0	0.5 *M* HCl + 1 *M* NH_4Cl	30
7	Hg(II)-Fe(III)	500 Hg	500 Hg	0	DMW	40
		125 Fe	123.3 Fe	−1.36	0.5 *M* HCl + 1 *M* NH_4Cl	40

shows a high reproducibility in its ion-exchange behavior and a crystalline nature with a d-value of 2.04 Å. When the material was heated at various temperatures ranging from 45 to 800°C for 1 h each, it was observed that up to 200°C the i.e.c. is lost only up to 4%. The solubility studies of this exchanger in various acids and alkali solutions suggest that it is quite stable in these media. The irradiation studies reveal that ZAS is stable under γ-radiations up to 38.4 Mrd.

The pH titration curves (Figs. 1 and 2) indicate an expected bifunctional behavior of the exchanger except for K^+ ions, for which a monofunctional behavior is observed. The second inflection for the sample ZAS, dried at room temperature, is at about 1.1 mmol of OH^- ions added, corresponds approximately to the experimentally obtained Na^+–i.e.c. of the material (Fig. 2). The samples heated at 200 or 400°C, however, lose their bifunctional characteristics, as is evident from Fig. 2. The IR spectrum of the ZAS sample (Fig. 4) shows sharp and strong bands at ~800, ~1600, and ~3500 cm^{-1} which justify the presence of arsenate, silicate, and external water molecules in the structure.

Distribution studies show a normally good selectivity of this material for various metal ions in water, which is usual for inorganic ion-exchangers. As it is clear from Fig. 5, the exchanger shows a reversal in K_d values for alkali metals on varying the pH. At pH ~ 0 the material shows the sequence $Cs^+ < K^+ < Na^+ < Rb^+$.

Thus it shows a maximum uptake for Rb^+ at this pH. However, at pH 1 the exchanger shows a high selectivity for Na^+ ions. At pH 7 a further reversibility is observed in its behavior, for there the exchanger shows a maximum affinity for Cs^+ ions. On the basis of distribution studies and individual elution curves of different metal ions, binary separations of Hg(II) from Cd(II), Pb(II), Ni(II), Co(II), Zn(II), Al(III), and Fe(III) have been successfully obtained, the details of which are summarized in Table 3. When a synthetic mixture containing Hg(II) and other metal ions (Cd, Pb, Ni, Co, Zn and Al) was loaded on its column, Hg(II) could be eluted out quantitatively in DMW. This study, therefore, points out the possibility of utilizing Zr(IV) arsenosilicate for some metal separations that are important from the pollution point of view. Analysis of rocks is another exciting application of this material. As Table 4 shows, quite satisfactory results are obtained within an experimental error of ±5%.

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TABLE 4

Quantitative Separation of Various Constituents in Rocks on ZAS Columns

No.		Volume of the stock solution loaded (mL)	Elements present as per the standard composition of the rock (μg)						Elements eluted out in various solvents (μg) (arrange values of three determinations). Eluants and their volumes		
			Al	Fe	Si	Ca	Mg	Mn	DMW (100 mL)	1 *M* HNO_3 (100 mL)	% Error for Al and Fe
1	G-2	0.5	7.70	1.35	34.61	0.98	0.375	0.020	Si (37.82) Ca (1.07) Mg (0.41)	Al (7.92) Fe (1.40)	Al +2.85 Fe +4.47
2	G-2	1.0	15.40	2.69	69.22	1.96	0.75	0.03	Si (74.11) Ca (2.02) Mg (0.79)	Al (15.8) Fe (2.76)	Al +2.59 Fe +2.60
3	AGV-1	0.5	8.60	3.89	29.81	2.47	0.76	0.05	Si (33.4) Ca (2.52) Mg (0.81) Mn (0.08)	Al (8.63) Fe (3.82)	Al +0.46 Fe −1.79
4	AGV-1	1.0	17.19	7.78	59.61	4.94	1.52	0.10	Si (64.15) Ca (5.04) Mg (1.64) Mn (1.01)	Al (17.4) Fe (7.7)	Al +1.22 Fe −1.02

5	BHVO-1	0.5	6.85	6.00	2.45	7.7	3.60	0.08	Si (2.45) Ca (7.81) Mg (3.39) Mn (0.08)	Al (6.96) Fe (6.16)	Al +1.6 Fe +2.66
6	BHVO-1	1.0	13.7	12.0	4.9	15.4	7.20	0.17	Si (5.18) Ca (15.65) Mg (7.32) Mn (0.16)	Al (14.2) Fe (11.85)	Al +3.64 Fe −1.25
7	BCR-1	0.5	6.86	6.71	27.26	3.48	1.74	0.09	Si (26.95) Ca (3.56) Mg (1.84) Mn (0.08)	Al (7.1) Fe (6.74)	Al +3.49 Fe +0.01
8	BCR-1	1.0	13.72	13.41	54.53	6.97	3.48	0.18	Si (13.84) Ca (6.88) Mg (3.37) Mn (0.16)	Al (13.96) Fe (13.62)	Al +1.74 Fe +1.56
9	PCC-1	0.5	0.36	4.14	21.05	0.27	21.75	0.06	Si (22.34) Ca (0.4) Mg (22.2) Mn (0.08)	Al (0.35) Fe (4.11)	Al −2.77 Fe −0.72
10	PCC-1	1.0	0.73	8.28	42.1	0.55	43.5	0.12	Si (44.7) Ca (0.83) Mg (44.15) Mn (0.14)	Al (0.72) Fe (8.14)	Al −1.36 Fe −1.69

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