

Re-evaluation and re-classification of erionite series minerals

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Abstract Governments and industries have introduced regulatory measures requiring safety controls to limit asbestos exposure of the general public and asbestos workers. Although erionite is a more potent health hazard mineral than asbestos, it has received far less attention. Precise definition of erionite, types of these fibrous minerals, and most importantly, characterization requirements still raise questions and often lead to arguments and even legal disputes. Many bulk erionite samples used in animal and cell experiments for carcinogenicity are not mineralogically pure. To test this hypothesis, we characterized two erionite standards from Rome, Oregon, and Pine Valley, Nevada, USA. These standards were characterized quantitatively using modern analytical techniques, and one of them, the erionite standard

from Rome, Oregon, passed the required tests for positive identification, but the other, the erionite standard from Pine Valley, Nevada, did not. Furthermore, we observed ambiguous definitions, incorrect identifications, and inaccurate reporting of clinical investigations. To address this problem, we established characterization guidelines for positive identification of erionite using a modified balance error formula, and we re-evaluated and re-classified published erionite data from the literature as erionite-Ca, erionite-Na, and erionite-K. If data did not pass either the E% or Mg-content test, then we propose that reference to them in the literature be disregarded. Erionite requires special attention from the mineralogical community to help establish its true carcinogenetic properties. We believe that the characterization guidelines established in this paper will contribute to setting up rules and regulations for evaluation of erionite by regulatory agencies.

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Introduction

Erionite, a zeolite group mineral, was first found in Durkee, Oregon, USA, and was defined by Eakle (1898) from materials sent to Harvard University. Erionite has been reported from many locations,

including Antarctica (Vezzalini et al. 1994), Austria (Waltinger and Zirkl 1974), Canada (Tschernich and Wise 1982), Czechoslovakia (Rychly et al. 1982), Faroe Islands (Hey 1959), France (Sheppard and Gude 1969a; Pongiluppi 1976), Georgia (Batiashvili and Gvakharia 1968), Germany (Rinaldi et al. 1975; Rinaldi 1976; Betz and Hentschel 1978; Hentschel 1986), Iceland (Metropolis 1986), Italy (Passaglia and Galli 1974; Passaglia et al. 1974), Japan (Harada et al. 1967; Shimazu and Kawakami 1967; Shimazu and Mizota 1972; Matsubara et al. 1978; Yamamoto et al. 1980), Kenya (Surdam and Eugster 1976), Korea (Noh and Kim 1986), New Zealand (Sameshima 1978; Aldridge and Pope 1981), Russia (Belitskiy and Bukin 1968), Scotland (Macpherson and Livingstone 1982), Tanzania (Surdam and Sheppard 1978), and Turkey (Mumpton 1979; Dogan 2003; Dogan et al. 2006). In the USA, several states have erionite deposits, including Arizona (Kamb and Oke 1960; Wise and Tschernich 1976; Thomssen 1983), California (Sheppard and Gude 1965, 1969b), Idaho (Reed 1937), Nevada (Deffeyes 1959; Papke 1972; Barrows 1980; Gude and Sheppard 1981), Oregon (Eakle 1898; Staples 1957; Staples and Gard 1959; Kamb and Oke 1960; Wise and Tschernich 1976, 1978; Howard 1978; Sheppard et al. 1983), Washington (Kamb and Oke 1960; Raymond and Tillson 1968; Wise and Tschernich 1976; Ames 1980), and Wyoming (Deffeyes 1959; Honda and Muffler 1970; Bargar et al. 1981). Erionite is not known to have been mined or marketed for commercial purposes since 1987. Where it has been used, or proposed for use, natural erionite has now been replaced by synthetic non-fibrous zeolites (IARC 1987a, b; EPA-US 1988).

Erionite in the Cappadocia region of Turkey was found to be the causative agent for the mesothelioma endemic in the region (Baris et al. 1978, 1979; Artvinli and Baris 1979). In 1987, IARC reported that there was sufficient evidence for its carcinogenicity in experimental animals. Additional evidence emerged when erionite fibers were found in the lung tissues of pleural mesothelioma cases from three villages in the Cappadocia region of Turkey, where there is an extremely high level of mortality from malignant mesothelioma. In consequence, erionite has been listed as carcinogenic to humans. In 1997, erionite was elevated to series status and individual types of erionite-Ca, erionite-Na, and erionite-K have since been defined (Coombs et al. 1997).

Many bulk erionite samples used in animal and cell experiments for carcinogenicity are not mineralogically pure. To prove this, we obtained and characterized two different erionite standards from the United States, one from Rome, Oregon; and the other from Pine Valley, Nevada. These samples were characterized quantitatively using modern analytical techniques.

We observed ambiguous definitions, incorrect identifications, and inaccurate reporting of clinical investigations. To address this problem, we established characterization guidelines for positive identification of erionite and re-evaluated and re-classified published erionite data from the literature.

Our re-calculation of Eakle's (1898) original result shows that the mineral erionite was correctly characterized in terms of balance error (E%) and Mg tests. However, erionite in the medical literature has often been incompletely or incorrectly characterized, thereby throwing doubt on the results of the work. Animal and cell experiments for the toxicity of erionite should only be performed with mineral samples that have passed the quantitative characterization tests (both E% and Mg-content), and the type of erionite (-Ca, -Na, -K) must be identified properly. Failure to do so makes the results of the experiments problematic and subject to controversy.

Materials and methods

Materials used in this study include two standard erionite samples; one from Rome, Oregon (CBES-6120), and the other from Pine Valley, Nevada, USA (CBES-6119). These erionite standards were characterized quantitatively using optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), powder X-ray diffraction (XRD), and inductively coupled plasma-mass spectrometry (ICP-MS) techniques.

OM was used to observe presence of fibrous materials, and high resolution SEM was used to determine the morphology (size, shape) of the fibrous minerals. SEM equipped with EDS was used to test elemental composition of the mineral, and powder XRD was used to verify mineralogy of the fibrous particles. The results were verified by ICP-MS at a certified laboratory (ACME Analytical Laboratories, Vancouver, BC, Canada) to check elemental composition of the fibrous minerals.

We used the results of ICP analyses to compute the balance error ($E\%$), and the Mg-content test was performed to verify the reliability of erionite. Minerals which passed both $E\%$ and Mg-content tests were re-evaluated and re-classified. Furthermore, published erionite data were obtained and re-evaluated and re-classified using the modified formula of $E = [(Al + Fe^{3+}) - (Na + K) + 2(Ca + Mg)] / [(Na + K) + 2(Ca + Mg)] \times 100$ with the boundary conditions of $\pm 10\%$ along with the Mg test ($Mg < 0.80$). Erionite which passed both tests were tabulated as erionite-Ca, erionite-Na, erionite-K. If data did not pass either of the tests then we propose that reference to them in the literature be disregarded.

Characterization guidelines

Erionite is almost certainly the most toxic naturally occurring fibrous mineral known. In consequence, quantitative characterization is extremely important. Samples should be characterized by using one or more of the following techniques:

- I. Group techniques for single fiber mineral analysis include
 - (i) Phase contrast microscopy (PCM) and/or optical microscopy (OM),
 - (ii) Scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) and/or wavelength dispersive spectroscopy (WDS),
 - (iii) Transmission electron microscopy (TEM) equipped with EDS and/or WDS, and selected area electron diffraction (SAED),
 - (iv) Electron probe micro analysis (EPMA).

Similar or better analytical techniques are acceptable.

- II. Group techniques for bulk mineral analysis include
 - (i) Powder X-ray diffraction (XRD) where there is a sufficient quantity of the sample,
 - (ii) Inductively coupled plasma-mass spectroscopy (ICP-MS) of enriched or purified erionite,
 - (iii) X-ray fluorescence (XRF) of enriched or purified erionite.

Similar or better analytical techniques are acceptable.

For the second group of analyses, samples should represent the entire set of bulk samples; must not have any contamination, and must be verified by other techniques (e.g., SEM to check if there are any impurities or contamination).

- III. Group computation includes chemical and structural characterization of erionite and verification of crystal chemistries by elemental distribution within the crystal. The crystal chemistry of erionite should be computed based upon the guidelines established by the IMA Zeolite Report of 1997. The reliability of the crystal chemistries of these erionites should be evaluated using the balance error formula

$$E = \frac{[(Al + Fe^{3+}) - (Na + K) + 2(Ca + Mg + Sr + Ba)]}{[(Na + K) + 2(Ca + Mg + Sr + Ba)]} \times 100.$$

Results of chemical analyses of erionite are only considered to be reliable if the balance error ($E\%$) is equal to or less than 10% (Passaglia 1970). If the computation is outside the boundary condition ($> \pm 10\%$) then the mineral is not erionite. However, if the computation is within the boundary conditions, the mineral may be erionite, or may be one of the other zeolite group minerals (i.e., clinoptilolite), which have similar elemental composition and structure and follow the similar rules.

In the crystal chemistries of erionite, Mg^{2+} cations can be present up to 0.80 atoms per cell (Gualtieri et al. 1998). If not, the mineral may not be erionite. The total of Si + Al [$+Fe^{3+}$] should be approximately equal to 36 atoms based upon 72 oxygen atoms in the erionite formula, although the Si/Al ratio alone cannot be used for identification (Dogan et al. 2005).

Results

In this study, we characterized two erionite standards from Rome, Oregon, and Pine Valley, Nevada, USA. These standards were characterized quantitatively using OM, SEM equipped with EDS, powder XRD, and the results verified by ICP-MS.

Figure 1a and b shows representative SEM images of the erionite standard from Rome, Oregon, USA, and Fig. 2a and b shows representative SEM images of the erionite standard from Pine Valley, Nevada, USA. Accelerating voltage was 5 kV, the bar scale

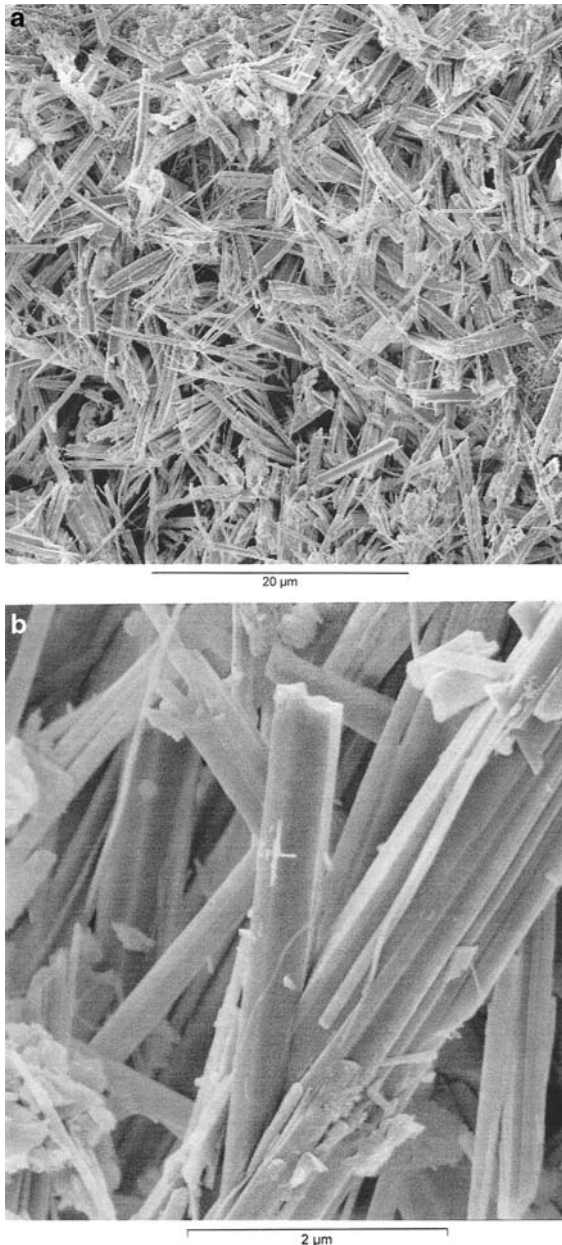


Fig. 1 (a, b) SEM images of the erionite standard from Rome, Oregon, USA (CBES-6120). Accelerating voltage = 5 kV, *bar scale* = 20 μm (a) and 2 μm (b), respectively. Note that individual erionite fibers are long and hexagonal in shape, and about 0.5 μm thick

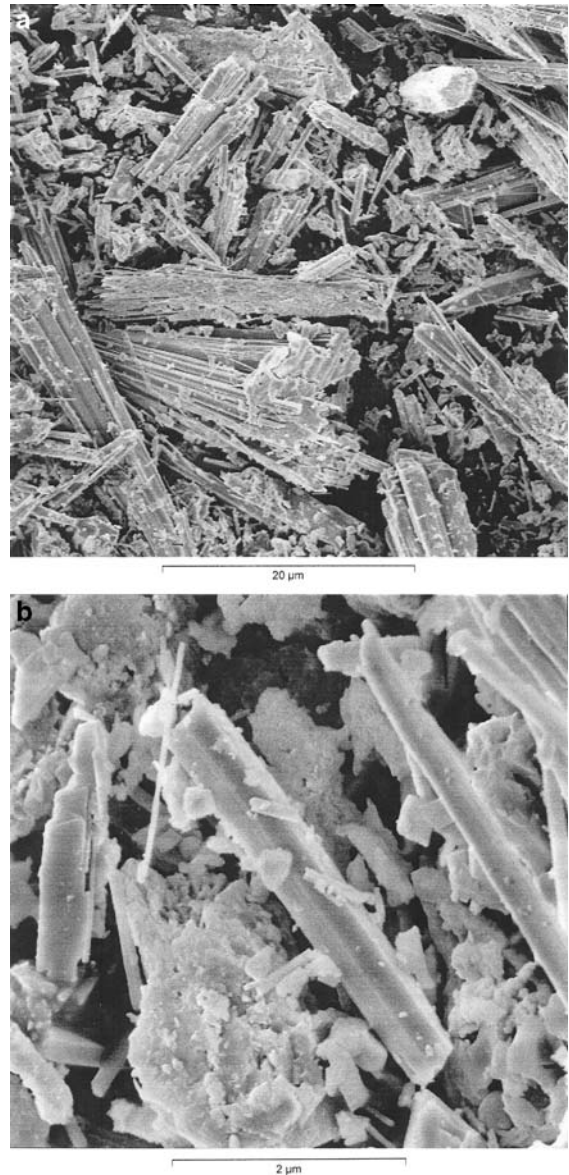


Fig. 2 (a, b) SEM images of the erionite standard from Pine Valley Nevada, USA (CBES-6119). Accelerating voltage = 5 kV, *bar scale* = 20 μm (a) and 2 μm (b), respectively. Note that individual erionite fibers are long and hexagonal in shape, and about 0.5 μm thick. Compared to the Oregon erionite standard, the Nevada erionite standard has a more “dusty” appearance

was 20 μm for Figs. 1a and 2a, and 2 μm for Figs. 1b and 2b, respectively.

The results of the erionite standard from Rome, Oregon, USA, passed both the E% and Mg tests, and were classified as erionite-K. However, the erionite

Table 1 The result of elemental distribution in the crystal chemistry of the erionite standards from Rome, Oregon, USA (CBES-6120), and Pine Valley, Nevada, USA (CBES-6119)

Location	Ca	Na	K	Mg	Si	Al	Fe	E%
Rome, Oregon, USA	0.82	1.93	2.76	0.77	27.93	6.68	1.17	-0.25
Nevada, USA	5.56	0.64	1.73	1.41	26.41	6.47	0.73	-55.82
Nevada, USA	5.54	0.65	1.88	1.70	26.39	6.47	0.73	-56.15

The chemical analyses were performed using ICP-MS technique

standard from Pine Valley, Nevada, USA, did not pass the tests. Table 1 shows results of elemental distribution in the crystal chemistry of the erionite standards from Rome, Oregon, and Pine Valley, Nevada, USA.

Chemical and structural characterization of erionites

The reliabilities of the crystal chemistries of these erionites have been evaluated using the formula of

$$E = \frac{[(Al + Fe^{3+}) - (Na + K) + 2(Ca + Mg + Sr + Ba)]}{[(Na + K) + 2(Ca + Mg + Sr + Ba)]} \times 100$$

with boundary conditions of ±10%. However, Ba and Sr are usually very minor components of the mineral

composition and have a negligible effect on the result. Therefore, a new modified formula

$$E = \frac{[(Al + Fe^{3+}) - (Na + K) + 2(Ca + Mg)]}{[(Na + K) + 2(Ca + Mg)]} \times 100$$

is proposed with the boundary conditions of ±10%.

Mg²⁺ content of these erionites has been evaluated with the passing value of Mg < 0.80. Erionites which passed both E% and Mg tests have been re-classified as erionite-Ca, erionite-Na, or erionite-K, according to the major cation contents.

Re-evaluation and re-classification of published data of erionites

The published data from different locations of the world were rigorously tested by first computing crystal chemistries of the erionites based upon 72 oxygens and then computing E% and Mg contents. Only the results which passed both tests were used to positively identify the erionite series minerals. Finally, the individual species (erionite-Ca, -Na, -K) were identified.

Positively identified erionite-Ca

Erionites from Shourdo, Georgia (Batiashvili and Gvakhariya 1968), Durkee, Oregon, USA (Sheppard

Table 2 The result of elemental distribution in the crystal chemistry of erionite-Ca, which passed both the balance error and Mg-content tests

Location	Ca	Na	K	Mg	Si	Al	Fe	E%	References
Beach Creek, Oregon, USA	4.36	0.14	1.94	0.41	24.48	11.47	0.00	-1.90	Sheppard et al. (1974)
British Columbia, Canada	3.90	0.19	2.12	0.10	25.27	10.82	0.00	3.74	Wise and Tschernich (1976)
Faedo, Vicenza, Italy	3.48	0.30	1.62	0.04	26.56	9.57	0.00	5.91	Passaglia and Tagliavini (1995)
Montresta, Nuoro, Italy	3.75	0.28	2.01	0.42	25.16	10.88	0.01	1.99	Passaglia et al. (1974)
Ballyclare, N. Ireland	3.99	0.10	2.14	0.35	25.13	10.84	0.00	-0.87	Passaglia et al. (1998)
Bog Hill Quarry, N. Ireland	2.90	0.03	1.76	0.41	27.17	8.88	0.08	6.23	Passaglia et al. (1998)
Lady Hill Quarry, N. Ireland	4.25	0.21	2.24	0.03	24.96	11.03	0.00	-0.30	Passaglia et al. (1998)
Island of Skye, Scotland	3.56	0.29	2.10	0.35	25.58	10.48	0.01	2.60	Passaglia et al. (1998)
Nizhnyaya Tunguska, Russia	3.77	0.06	1.69	0.07	26.40	9.60	0.04	1.61	Belitskiy and Bukin (1968)
Shourdo, Georgia	2.42	0.15	2.02	0.53	27.59	8.51	0.01	5.64	Batiashvili and Gvakhariya (1968)
Jindivick, Australia	3.73	0.75	2.03	0.24	24.67	11.52	0.00	6.77	Birch (1987)
Merriwa, Australia	4.11	0.15	1.97	0.51	24.57	11.42	0.00	-0.07	England and Ostwald (1979)
Mean	3.56	0.27	1.95	0.30	25.78	10.28	0.01	2.82	

and Gude 1969a), Beach Creek, Oregon, USA (Sheppard et al. 1974), Montresta, Nuoro, Italy (Passaglia et al. 1974), British Columbia, Canada (Wise and Tschernich 1976), Montecchio Maggiore, Italy (Giovagnoli and Boscardin 1979), Merriwa, Australia (England and Ostwald 1979), Jindivick, Australia (Birch 1987), Phillip Island, Australia (Birch 1988), Faedo, Vicenza, Italy (Passaglia and Tagliavini 1995), Nizhnyaya Tunguska, Russia (Belitskiy and Bukin 1968) and Ballyclare, Bog Hill Quarry, Lady Hill Quarry, N. Ireland; Island of Skye, Scotland (Passaglia et al. 1998) passed both the E% and Mg-content tests and were re-classified as erionite-Ca.

A formula for erionite-Ca has been established using the mean values of elements from these recomputed analyses. This new general formula proposed for those erionite-Ca samples is: $(Ca_{3.56}^{2+}K_{1.95}^{+}Na_{0.27}^{+}Mg_{0.30}^{2+})(Si_{25.78}Al_{10.28}Fe_{0.01}^{3+})O_{72}$.

Table 2 shows the result of re-classified erionite-Ca for samples, which passed both the E% and Mg-content tests.

Positively identified erionite-Na

Erionites from Durkee, Oregon, USA (Eakle 1898), Cady Mountains, California, USA (Sheppard and Gude 1965), Lake Natron, Tanzania (Hay 1966), Crooked Creek, Oregon, USA (Sheppard and Gude 1969a), Phillip Island and Cairns Bay, Australia (Birch 1988), Campbell Glacier, Antarctica (Vezzalini et al. 1994), Mt. Adamson, Antarctica (Vezzalini

et al. 1994), Dunseverik, N. Ireland (Passaglia et al. 1998), Montecchio, Maggiore, Italy (Passaglia et al. 1998), and some samples from the Cappadocia region of Turkey (Dogan et al. 2006) passed both the E% and Mg-content tests and were re-classified as erionite-Na.

A formula for erionite-Na has been established using the mean values of elements from these recomputed analyses. This new general formula proposed for the erionite-Na samples is: $(Na_{4.00}^{+}K_{2.40}^{+}Ca_{1.13}^{2+}Mg_{0.24}^{2+})(Si_{26.69}Al_{9.11}Fe_{0.22}^{3+})O_{72}$.

Table 3 shows the result of re-classified erionite-Na for samples, which passed both the E% and Mg-content tests.

Positively identified erionite-K

Erionites from Durkee, Oregon, USA (Staples and Gard 1959), Rome, Oregon, USA (Eberly 1964), Yaquina Head, Oregon, USA (Wise and Tschernich 1976), Reese River, Nevada, USA (Gude and Sheppard 1981), Ortenberg Quarry, Germany (Hentschel 1986), Rome, Oregon, USA, and some samples from the Cappadocia region of Turkey (Dogan et al. 2006) passed both the E% and Mg-content tests and were re-classified as erionite-K.

A formula for erionite-K has been established using the mean values of elements from these recomputed analyses. This new general formula proposed for the erionite-K samples is: $(K_{2.80}^{+}Na_{1.66}^{+}Ca_{1.03}^{2+}Mg_{0.51}^{2+})(Si_{28.21}Al_{7.39}Fe_{0.41}^{3+})O_{72}$.

Table 3 The result of elemental distribution in the crystal chemistry of erionite-Na, which passed both the balance error and Mg-content tests

Location	Ca	Na	K	Mg	Si	Al	Fe	E%	References
Crooked Creek, Oregon, USA	0.65	3.15	2.58	0.34	28.20	7.33	0.46	1.01	Sheppard and Gude (1969a)
Cady Mountains, California, USA	0.11	5.51	1.98	0.18	27.90	7.47	0.54	-0.71	Sheppard and Gude (1965)
Dunseverik, N. Ireland	0.89	5.20	2.73	0.26	25.07	11.10	0.01	7.23	Passaglia et al. (1998)
Lake Natron, Tanzania	0.00	5.78	2.50	0.11	27.33	7.84	0.71	0.70	Hay (1966)
Cairns Bay, Australia	1.33	5.46	2.44	0.36	24.63	11.24	0.16	0.78	Birch (1988)
Campbell Glacier, Antarctica	1.43	2.70	2.12	0.57	27.21	8.47	0.30	-0.74	Vezzalini et al. (1994)
Mt. Adamson, Antarctica	2.25	2.66	2.17	0.07	26.32	9.71	0.02	2.30	Vezzalini et al. (1994)
Mt. Adamson, Antarctica	2.51	3.33	2.14	0.06	25.49	10.46	0.01	-1.72	Vezzalini et al. (1994)
Tuzkoy, Turkey	0.87	2.63	2.11	0.38	29.05	6.35	0.41	-6.53	Dogan et al. (2006)
Mean	1.13	4.00	2.40	0.24	26.69	9.11	0.22	1.43	

Table 4 The result of elemental distribution in the crystal chemistry of erionite-K, which passed both the balance error and Mg-content tests

Location	Ca	Na	K	Mg	Si	Al	Fe	E%	References
Rome, Oregon, USA	0.75	1.67	4.14	0.54	27.54	7.25	1.24	1.26	Eberly (1964)
Yaquina Head, Oregon, USA	1.18	1.47	2.72	0.74	27.57	8.57	0.00	6.86	Wise and Tschernich (1976)
Reese River, Nevada, USA	1.69	1.00	2.84	0.30	27.83	8.18	0.08	5.55	Gude and Sheppard (1981)
Ortenberg Quarry, Germany	0.99	2.31	3.32	0.06	28.01	8.05	0.01	3.87	Hentschel (1986)
Karain, Turkey	0.98	1.95	2.18	0.41	29.06	6.33	0.49	-0.27	Dogan et al. (2006)
“Old” Sarihidir, Turkey	0.93	1.48	2.22	0.55	28.82	6.78	0.45	8.33	Dogan et al. (2006)
Karlik, Turkey	0.48	1.81	2.98	0.40	29.70	5.88	0.28	-5.92	Dogan et al. (2006)
Mean	1.03	1.66	2.80	0.51	28.21	7.39	0.41	3.27	

Table 5 The result of elemental distribution in the crystal chemistry of erionite-Ca, which failed either the balance error or Mg-content tests

Location	Ca	Na	K	Mg	Si	Al	Fe	E%	References
Agate Beach, Oregon, USA	2.42	0.18	1.77	0.82	27.17	8.92	0.03	5.44	Wise and Tschernich (1976)
Oregon, USA	1.61	0.37	1.08	0.58	28.25	8.23	0.00	41.14	Poole et al. (1983)
Araules, Ht Loire, France	3.72	0.03	2.18	0.83	24.54	11.41	0.00	-1.69	Pongiluppi (1976)
Maze, Niigata Prefecture, Japan	2.28	0.95	1.54	0.86	26.90	8.83	0.38	5.18	Harada et al. (1967)
Karain, Turkey (Karain-I)	2.31	0.22	0.74	0.57	28.11	7.99	0.00	18.69	Pooley (1979)
Karain, Turkey (Karain-III)	1.44	0.30	0.59	1.49	27.73	8.39	0.00	24.19	Pooley (1979)
Turkey (erionite-I)	1.54	0.00	0.65	0.48	28.70	7.98	0.00	69.83	Suzuki and Kohyama (1984)

Table 4 shows the result of re-classified erionite-K for samples, which passed both the E% and Mg-content tests.

Undifferentiated erionites

In some cases, different results have been reported for erionites from the same locations by different authors. If data do pass both tests, but are characterized as from more than one type of erionites, then the mineral should be classified as “undifferentiated” erionite until there has been further clarification. For example, Italian samples reported from Montecchio (Giovagnoli and Boscardin 1979; Passaglia et al. 1998) were re-calculated as erionite-Ca and erionite-Na, respectively. Two sets of data from Phillip Island, Australia (Birch 1988) were re-calculated as both erionite-Ca and erionite-Na. Data from Durkee, Oregon, USA by three different authors (Sheppard and Gude 1969a; Eakle 1898; and Staples and Gard 1959) were re-calculated and found to be erionite-Ca, erionite-Na, erionite-K, respectively.

Disregarded erionites

If data do not pass either the E% or Mg-content test or neither, then reference to them in the literature should be disregarded.

Table 5 shows the results of re-classified erionite-Ca samples, which failed either the E% or Mg-content tests.

Table 6 shows the results of re-classified erionite-Na samples, which failed either the E% or Mg-content tests.

Table 7 shows the results of re-classified erionite-K samples, which failed either the E% or Mg-content tests.

Discussion and conclusions

It is interesting to note that one of the two standard erionites analyzed, which were used in animal and cell experiments, did not pass the proposed tests. This clearly indicates that quantitative mineralogical tests

Table 6 The result of elemental distribution in the crystal chemistry of erionite-Na, which failed either the balance error or Mg-content tests

Location	Ca	Na	K	Mg	Si	Al	Fe	E%	References
Bowie, Arizona, USA	0.77	3.93	2.41	0.75	28.02	7.02	0.47	-20.30	Tsitsishvili et al. (1992)
Lake Tecopa, California, USA	0.32	3.95	2.42	0.75	28.16	7.06	0.50	-11.34	Sheppard and Gude (1969b)

Table 7 The result of elemental distribution in the crystal chemistry of erionite-K, which failed either the balance error or Mg-content tests

Location	Ca	Na	K	Mg	Si	Al	Fe	E%	References
Oregon, USA	1.09	0.40	1.63	0.91	28.74	7.44	0.00	23.62	Dumortier et al. (2001)
Jersey Valley, Nevada, USA	1.36	0.59	2.93	0.82	27.92	7.95	0.14	2.80	Sheppard and Gude (1969a)
Nevada, USA	0.86	1.56	3.65	2.77	27.27	6.73	0.51	-44.88	Tsitsishvili et al. (1992)
Karain, Turkey	0.59	0.91	2.89	0.87	28.89	7.09	0.00	5.54	Poole et al. (1983)
Tuzkoy, Turkey (BAL fibers)	0.18	2.11	2.25	0.28	28.73	7.71	0.00	45.97	Dumortier et al. (2001)
Tuzkoy, Turkey (soil)	0.91	1.57	3.79	0.61	28.30	7.29	0.00	-13.19	Dumortier et al. (2001)
Tuzkoy, Turkey	0.33	1.20	2.03	0.00	27.87	9.28	0.00	138.14	Sebastien et al. (1981)
Tuzkoy, Turkey	0.33	0.60	2.43	0.06	28.45	8.65	0.00	126.97	Sebastien et al. (1981)
Turkey (erionite-II)	1.10	0.00	1.43	0.97	28.50	8.04	0.00	44.01	Suzuki and Kohyama (1984)

should be performed on these standards before being used in vivo or in vitro laboratory experiments. Furthermore, data from the literature have allowed us to up-date descriptions of erionite to the standards of modern classification.

The followings are the results and suggestions from this study:

- (i) The reliability of the crystal chemistries of these erionites have been evaluated using the new modified E% formula

$$E = \frac{[(Al + Fe^{3+}) - (Na + K) + 2(Ca + Mg)]}{[(Na + K) + 2(Ca + Mg)]} \times 100$$

with the boundary conditions of $\pm 10\%$. The Mg content of these erionites has been evaluated with the passing value of $Mg < 0.80$.

- (ii) Some erionite data in the literature did not pass either the E% test or Mg-content test or neither. As a result, these data could not be accepted as erionite, and reference to them in the literature should be disregarded.
- (iii) Erionites from: Shourdo, Georgia; Beach Creek, Oregon, USA; Montresta, Nuoro, and Faedo, Vicenza, Italy; British Columbia, Canada; Jindivick and Merriwa, Australia; Ballyclare, Bog Hill Quarry, Lady Hill Quarry, N. Ireland;

Island of Skye, Scotland; and Nizhnyaya, Tunguska, Russia passed both the E% and Mg-content tests and were re-classified as erionite-Ca. A new general formula $(Ca_{3.56}^{2+}K_{1.95}^{+}Na_{0.27}^{+}Mg_{0.30}^{2+})(Si_{25.78}Al_{10.28}Fe_{0.01}^{3+})O_{72}$ is proposed for the erionite-Ca.

- (iv) Erionites from Cady Mountains, California, USA; Lake Natron, Tanzania; Crooked Creek, Oregon, USA; Campbell Glacier and Mt. Adamson, Antarctica; Dunseverik, N. Ireland; Cairns Bay, Australia; and Tuzkoy, Turkey passed both the E% and Mg-content tests and were re-classified as erionite-Na. A new general formula $(Na_{4.00}^{+}K_{2.40}^{+}Ca_{1.13}^{2+}Mg_{0.24}^{2+})(Si_{26.69}Al_{9.11}Fe_{0.22}^{3+})O_{72}$ is proposed for the erionite-Na.
- (v) Erionites from Rome, Oregon, USA; Yaquina Head, Oregon, USA; Reese River, Nevada, USA; Ortenberg Quarry, Germany and Karain, "Old" Sarihidir, Karlik, Turkey passed both the E% and Mg-content tests and were re-classified as erionite-K. A new general formula $(K_{2.80}^{+}Na_{1.66}^{+}Ca_{1.03}^{2+}Mg_{0.51}^{2+})(Si_{28.21}Al_{7.39}Fe_{0.41}^{3+})O_{72}$ is proposed for the erionite-K.
- (vi) Samples from Italy reported from Montecchio were re-calculated as both erionite-Ca (E% = 6.16) and erionite-Na (E% = 6.08).

Two sets of data from Phillip Island, Australia were re-calculated as both erionite-Ca ($E\% = 5.84$) and erionite-Na ($E\% = 7.54$). Data from Durkee, Oregon, USA by three different authors were re-calculated and found to be erionite-Ca ($E\% = -1.02$), erionite-Na ($E\% = 1.16$), erionite-K ($E\% = 10.0$), respectively. Thus, until further clarification, these samples have been classified as undifferentiated erionites.

- (vii) Erionites from Bowie, Arizona, USA, and Lake Tecopa, California, USA, were classified as erionite-Na. However, $E\%$ of these erionites were calculated as -20.30 and -11.34 , respectively. Erionite from Oregon, USA was classified as erionite-Ca. However, $E\%$ of this erionite was calculated as 41.14 . Therefore, these samples did not pass the $E\%$ test and cannot be classified as erionite.
- (viii) Erionites from Karain, Turkey, were classified as erionite-Ca. However, $E\%$ of these erionites were calculated as 18.69 and 24.19 for Karain-I and Karain-III samples, and 69.83 for erionite-I sample, respectively. Erionites from Tuzkoy, Turkey were classified as erionite-K. However, $E\%$ of these erionites were calculated as 45.97 and -13.19 for fibers from bronchoalveolar lavage and a soil sample, and 138.14 and 126.97 for sample-I and sample-II, respectively. Thus, these samples did not pass the $E\%$ test and cannot be classified as erionite.
- (ix) Mg contents of erionite-Ca from Agate Beach, Oregon, USA, and Araules, Ht Loire, France, were calculated as 0.82 and 0.83 , respectively. Mg contents of erionite-K from Jersey Valley, Nevada, USA, and Karain, Turkey, were calculated as 0.82 and 0.87 , respectively. Thus, these samples did not meet the requirement of $Mg < 0.80$.
- (x) The composition of the type specimen of erionite-Ca from Maze, Niigata, Japan, has a level more than the acceptable 0.80 Mg in the crystal structure. Furthermore, the $(Na + K) > (Ca + Mg)$ condition is not satisfied. Therefore, the type specimen of erionite-Ca should be replaced with a more suitable standard.
- (xi) Erionite-K from Oregon, USA, Nevada, USA, and Cappadocia, Turkey (erionite-II), did not pass either the $E\%$ test ($23.62, -44.88, 44.01$) or the Mg-content test ($0.91, 2.77, 0.97$), respectively. Thus, these samples cannot be classified as erionite.
- (xii) Certain locations of the Cappadocia region, Turkey, have the highest rate of malignant mesothelioma known in their population, and most of the human erionite data has come from this region. None of the published results of erionites before 2006 from the Cappadocia region passed the $E\%$ and Mg content tests. Dogan et al. (2006) showed that erionites from Tuzkoy have mean balance error ($E\%$) of -6.53 , and the type is erionite-Na; Karain, “Old” Sarihidir, and Karlik villages all have erionite-K with the mean balance errors of $-0.27, 8.33$, and -5.92 , respectively.
- (xiii) An attempt has been made to establish a data bank of erionites (Dogan and Dogan 2002). A data bank should be established under the auspices of one of the mineralogical societies. The new data must be evaluated rigorously before being accepted into the data bank. Data should be updated periodically and be available to the medical and mineralogical research communities.
- (xiv) There have been biological experiments performed using these uncharacterized erionite specimens. Animal and cell experiments should be performed only with minerals that have passed the quantitative characterization tests. Since the positive mineralogical identification, both for single fiber and bulk mineral, is very important, we suggest that the characterization guidelines described in this paper should be followed closely.
- (xv) Unlike other minerals, erionite requires a special attention to help establish its true carcinogenetic properties; and characterization requirements proposed in this paper will contribute setting up rules and regulations for erionite by the regulatory agencies.

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